

Appendix A

Thermodynamics, Large Numbers and the Most Probable State

Thermodynamics deals with systems with very large number of atoms. For instance, four grams of Helium have approximately 6×10^{23} molecules.¹ Considering that the age of the Universe is only about 5×10^{17} s, this is a very large number.

Inter-particle interactions make exact analysis of most thermodynamic systems well nigh impossible. Indeed, when theoretical formulation is used – as, for example, is done within the framework of Statistical Mechanics – approximations are often needed for its evaluation. Therefore, rather than getting involved with “a priori” calculations, thermodynamics generally deals with inter-relationships of physical properties of macroscopic systems. Because such knowledge can often help relate easily measurable properties to those that are hard to measure, thermodynamic plays an important role in scientific disciplines.

In this appendix, we show how large numbers, that are central to the validity of thermodynamic relationships, possess some simplifying properties. This fact is best demonstrated by analyzing an idealized model. Frequency moments of the exact distribution function as well as those of the relevant Gaussian approximation are worked out and the impressive validity of the Gaussian approximation is pointed out. Also, the helpful use of binomial expansion is noted. It is demonstrated that in a macroscopically large system, the most probable configuration is overwhelmingly so. Therefore, the result of any “macroscopic” measurement is well described by an accurate calculation of the most probable state.

A.1 Model

Random number generators are available in most mathematical software packages. When a “perfect random number generator” (PRNG) is set to return values within a “specified range” that extends, let us say, from $0 \rightarrow 1$, it does so with equal

¹Note, one He atom is a molecule.

probability for all values that lie within the range. And, if the PRNG were called an infinite number of times, the number density of returned values per unit microscopic length would be identically the same throughout the specified range $0 \rightarrow 1$.

Therefore, let us consider the following scenario. Some person wishes to use a PRNG to fill a group of N locations – to be called N “sites” – with a total of exactly $N\mu$ “occupied” sites² and $N(1 - \mu)$ “unoccupied” sites.³ A person might imagine that all that he/she needs to do is the following:

Catalogue every call returned by the PRNG into one of two possible statements: “occupied” or “unoccupied.”

Record that the i -th site is “occupied” if the i -th call returns a value somewhere between 0 and μ . Denote this fact by setting an occupancy variable $\sigma_i = 1$.

Otherwise, if the i -th call returns a value that lies between μ and 1, the i -th site is to be considered “unoccupied.” And this fact is to be denoted by setting the occupancy variable $\sigma_i = 0$.

For extreme simplicity, let us deal first with a trivial case. Assume that the total number of sites $N = 2$ and $\mu = 0.5$. So the number of occupied sites is equal to the number of un-occupied sites: both being equal to 1. Assume that we want to save effort and decide to make only 2 PRNG calls in the belief that the number of calls need not be much larger than the number of sites available. We ask the question: What is wrong with a person’s belief that the proposed arrangement, based on only two PRNG calls, will successfully result in fitting the two sites with exactly $N\mu = 1$ occupied, and $N(1 - \mu) = 1$ unoccupied, sites.

An incorrect answer would claim that, inasmuch as the statements about the PRNG returning calls between 0, $\frac{1}{2}$, and 1 do not specify what happens exactly at 0, $\frac{1}{2}$, and 1, the proposal given to the computer – that runs the PRNG – is vague. Hence, the difficulty!

The correct answer is that, unlike in a thermodynamic system, the number of calls is not “large.” Therefore, the fluctuations in the result are significant. And, hence there is a sizeable probability that the PRNG result for the number of occupied sites will turn out to equal 2 or 0, both very different from the actual number that is equal to 1.

A.2 Binomial Expansion

Determining the results of a large number of calls of the PRNG requires some effort. Fortunately, a little help from the binomial expansion does the trick. The binomial equality given below holds for finite values of the two given variables μ and μ_o .

²Important Notice: The symbol μ , which is mostly used for denoting the chemical potential, is temporarily being appropriated for use as the relative concentration of occupied sites.

³The present formulation also applies to a group of N , non-interacting, spins. Out of such a group, $N\mu$ spins are supposed to be pointing up so that each can be said to have a spin $s = +1$, and $N(1 - \mu)$ spins are pointing down so that each of their spins $s = -1$.

$$(\mu + \mu_o)^N = \sum_{p=0}^N \left[\frac{N!}{(p)!(N-p)!} \right] \mu^p \mu_o^{N-p}; \quad p = 0, 1, 2, \dots, N \quad (\text{A.1})$$

The above equality can conveniently be used to study the case where the total number of sites – and also the total number of the PRNG calls – is equal to N . To do this:

Set the variables μ and μ_o to represent the desired concentrations of the occupied and the un-occupied sites.⁴ Further, denote 100% concentration as equalling 1. Then we have

$$0 \leq \mu \leq 1; \quad 0 \leq \mu_o \leq 1; \quad \mu + \mu_o = 1. \quad (\text{A.2})$$

As a result, the left hand side of (A.1) is equal to unity. Therefore, $\left[\frac{N!}{(p)!(N-p)!} \right] \mu^p (1 - \mu)^{N-p}$ represents the probability that out of N sites, a number (p) will be found to be occupied and ($N-p$) will be found unoccupied. Note that according to (A.1) and (A.2), the sum of all such probabilities, i.e., where the number p of occupied sites ranges from 0 to N , is equal to unity: that is, it is a 100%.

A.2.1 Two Sites: A Trivial Example

As mentioned before, it is helpful to treat first the rather trivial case where the total number of sites, i.e., N , is very small: that is, $N = 2$. The two sites can be occupied in four different ways: meaning, four different combinations of the occupancy variables σ_1 and σ_2 are possible. For example, we can have:

$$\begin{aligned} \sigma_1 = 0, \quad \sigma_2 = 0 & ; \quad \sigma_1 = 1, \quad \sigma_2 = 1; \\ \sigma_1 = 1, \quad \sigma_2 = 0; \quad \sigma_1 = 0, \quad \sigma_2 = 1. \end{aligned} \quad (\text{A.3})$$

For simplicity, let us choose the desired value of the concentration, μ , of the occupied sites to be equal to 0.5.⁵

According to (A.1) the probability that two calls to the PRNG will actually lead to zero number of occupied sites – i.e., $p = 0$ – is

$$\left[\frac{N!}{(p)!(N-p)!} \right] \mu^p (1 - \mu)^{N-p} = \left[\frac{2!}{(0)!(2)!} \right] (0.5)^0 (0.5)^2 = \frac{1}{4}.$$

⁴Remember: We can immediately apply the present formulation and its results to the field-free, non-interacting, up-down spin problem. All that needs to be done is to replace the “occupied sites” by “up-spins” and the “un-occupied” sites by “down-spins.”

⁵When this is the case, these four combinations are all equally likely to occur. As such, they can be referred to as the four possible “micro-states” of the system. Note, the system consists of only two sites.

Similarly, if we set $p = 1$, we get the probability that the two calls to the PRNG will lead to only a single occupied site:

$$\left[\frac{N!}{(p)!(N-p)!} \right] \mu^p (1-\mu)^{N-p} = \left[\frac{2!}{(1)!(1)!} \right] (0.5)^1 (0.5)^1 = \frac{1}{2}.$$

And finally, the probability that the two calls to the PRNG will lead to exactly two occupied sites is found by setting $p = 2$.

$$\left[\frac{N!}{(p)!(N-p)!} \right] \mu^p (1-\mu)^{N-p} = \left[\frac{2!}{(2)!(0)!} \right] (0.5)^2 (0.5)^0 = \frac{1}{4}.$$

By the way, in order to get the relevant number of states, the above results for the probabilities need to be multiplied by $N^2 = 4$.⁶

We notice that in the small system being studied above, that has only $N = 2$ sites, and $2^N = 4$ states, the results given by the PRNG do not correspond well with our expressed desire. We had wanted the PRNG to return exactly 50% occupancy. This would have happened only if all the four states had contained exactly one occupied, and one un-occupied, site. Instead, what really happened is that out of four possible states, only two are of the desired variety. Of the other two states, the first contains no occupied sites: while the second, has both sites occupied. Accordingly, there is only a half-chance that, in practise, our expressed desire will actually be realized.

A physically more instructive description of the above happenstance is the following: The desired result is the most likely result.⁷ For a system that is not “large,”⁸ the desired result is still not overwhelmingly probable.⁹ One expects that things will improve if the number of calls, N , is “large.” Hopefully then the desired result will be overwhelmingly probable.¹⁰ This matter is investigated below.

A.3 Large Number of Calls

Let us, for the moment, continue to treat the simple case where the desired concentration, μ , of the occupied sites equals that of the un-occupied sites, $1 - \mu$. That is, $\mu = \frac{1}{2}$.

Consider a system with a very large number of sites, i.e., $N \gg 1$. As per the described procedure, this entails making a large number of calls – equal to N . To deal with this situation – see (A.1) – we need factorials of large numbers.

⁶Compare this prediction with the demonstration of the four possible states shown in (A.3).

⁷Note: While two states corresponded to the desired result, only one each referred to the un-desired, others.

⁸A system with only two sites is a “small” system.

⁹An event that has only half a chance of occurring is not considered to be a highly probable event.

¹⁰In other words, then the actual value returned by the PRNG will correspond much more closely to that which was desired.

When N is very large compared to unity, according to Stirling's zeroth-order approximation, the factorial of N can be approximated as follows:

$$N! \sim (N/e)^N. \quad (\text{A.4})$$

Insert this value of $N!$ into (A.1) and (A.2) and study the case where the actual number of occupied, p , and the unoccupied, $N - p$, sites is exactly equal to that suggested by the desired concentration of the occupied and the un-occupied sites: that is, $p = \mu N$ and $N - p = (1 - \mu)N$. Then, because μ has been chosen to be $\frac{1}{2}$ here, the probability of such occupancy is:

$$\begin{aligned} \left[\frac{N!}{(p)!(N-p)!} \right] \mu^p (1-\mu)^{N-p} &= \left[\frac{N!}{(N/2)!(N/2)!} \right] (1/2)^{N/2} (1/2)^{N/2} \\ &\sim \left[\frac{(N/e)^N}{(N/2e)^{N/2} (N/2e)^{N/2}} \right] (1/2)^{N/2} (1/2)^{N/2} \\ &= \left[\frac{(N/e)^N}{(N/2e)^N} \right] (1/2)^N = 1. \end{aligned} \quad (\text{A.5})$$

What a fantastic outcome! The result is exactly as was desired. Its probability of occurrence is a 100% and it occurs exactly at the desired place: namely, where the number of occupied and unoccupied sites is equal, i.e., they are both $N/2$. Accordingly, an infinitely narrow region must contain all the 2^N states of the model!

Is this really true? Or has the crudeness of the approximation for $N!$ – given in (A.4) – deceived us?

To investigate this matter further, it is necessary first to use a more accurate version of the Stirling asymptotic series. That is

$$N! = (2\pi N)^{1/2} (N/e)^N \left[1 + \frac{1}{12N} + \frac{1}{288N^2} + O\left(\frac{1}{N^3}\right) \right]. \quad (\text{A.6})$$

Inserting the above approximation for $N!$ into the right hand side of (A.5), readily yields the following result

$$\left[\frac{N!}{(N/2)!(N/2)!} \right] (1/2)^{N/2} (1/2)^{N/2} = \sqrt{(2/\pi N)} [1 + O(1/N)]. \quad (\text{A.7})$$

A.3.1 Exercise: I

Derive (A.7).

A.3.2 Large Number of Calls: Continued

Unlike the fantastic statement made by (A.5), (A.7) is quite sensible. All the states do not reside, exactly as desired, at $p = N/2$. Rather, in order to collect most of them, one would need to sum over a range of p values – i.e., the occupied sites – that are narrowly spread around the desired occupancy number $N\mu = N/2$. As a rough guess, as the above equation indicates, the width of such a region should be approximately equal to $\sqrt{(\pi N/2)}$. A more precise estimate of the size of the width is discussed below.

A.3.3 Remark: A Gaussian Distribution

An adequate estimate of the width of the distribution can be had by making a simple assumption that around the most probable location, i.e., at the desired value of the occupancy, the distribution of states has roughly a Gaussian shape.

As a physical test, for general value of the desired concentration μ , we carry out an exact calculation of several frequency moments of the distribution function. We find that these moments are well represented by a Gaussian approximation for the exact distribution function.

Moreover, as indicated below, the functional form of the density of states – for $\mu = \frac{1}{2}$ and very large N – also yields a result that is close to a Gaussian.

A.3.4 Gaussian Approximation for Region Around Half-Concentration

In order to calculate the probability that the occupancy closely ranges around the desired value, one needs to employ (A.1), or equivalently, the left-hand side of (A.5). Next, one sets $N \gg 1$, and chooses the desired concentration, μ , of the occupied sites. For instance, here we have chosen $\mu = 1 - \mu = 0.5$. In order to examine the region that lies immediately around the relevant occupancy number – i.e. $= \frac{N}{2}$ here – one needs to set $p = (\frac{N}{2} + n)$ and $N - p = (\frac{N}{2} - n)$ and remember to choose $n \ll N$.

Then, according to (A.1), the result for the probability distribution function is

$$\frac{N!}{(\frac{N}{2} + n)! (\frac{N}{2} - n)!} \left(\frac{1}{2}\right)^{(\frac{N}{2} + n)} \left(\frac{1}{2}\right)^{(\frac{N}{2} - n)}. \quad (\text{A.8})$$

Notice that the distribution is symmetric for the interchange $\pm n \rightarrow \mp n$. Moreover, when $(\frac{n^2}{N}) \ll 1$ the above can be expanded in powers of $(\frac{n^2}{N})$. That is,

$$\begin{aligned}
 & \frac{N!}{\left(\frac{N}{2} + n\right)! \left(\frac{N}{2} - n\right)!} \left(\frac{1}{2}\right)^{\left(\frac{N}{2} + n\right)} \left(\frac{1}{2}\right)^{\left(\frac{N}{2} - n\right)} \\
 &= \sqrt{\left(\frac{2}{\pi N}\right)} \cdot \left[1 - \left(\frac{2}{N} n^2\right) + \mathcal{O}\left\{\left(\frac{n^2}{N}\right)^2\right\} + \dots \right], \\
 &\approx \sqrt{\left(\frac{2}{\pi N}\right)} \cdot \exp\left(-\frac{2}{N} n^2\right). \tag{A.9}
 \end{aligned}$$

A.3.5 Exercise: II

Derive the relationships implicit in (A.9).

A.3.6 Gaussian Approximation: Continued

There were three good reasons why the expansion on the right-hand side of (A.9) was approximated by the exponential $\exp\left(-\frac{2}{N} n^2\right)$. First: Two leading terms agree. Second: The quadratic dependence on n is consistent with the symmetry, $n \pm \rightarrow n \mp$, of the left-hand side of (A.9). Three: The requirement

$$\begin{aligned}
 \left(\frac{1}{2} + \frac{1}{2}\right)^N &= \sum_{p=0}^N \left[\frac{N!}{(p)!(N-p)!} \right] \left(\frac{1}{2}\right)^p \left(\frac{1}{2}\right)^{N-p}, \quad p = 0, 1, 2, \dots, N \\
 &= 1, \tag{A.10}
 \end{aligned}$$

when translated by setting $p = \frac{N}{2} + n$ – as in (A.11) below –

$$\begin{aligned}
 \sum_{n=-\frac{N}{2}}^{n=+\frac{N}{2}} \frac{N!}{\left(\frac{N}{2} + n\right)! \left(\frac{N}{2} - n\right)!} \left(\frac{1}{2}\right)^{\left(\frac{N}{2} + n\right)} \left(\frac{1}{2}\right)^{\left(\frac{N}{2} - n\right)} &= 1 \\
 \approx \sqrt{\frac{2}{\pi N}} \cdot \int_{-\frac{N}{2}}^{+\frac{N}{2}} \exp\left(-\frac{2}{N} n^2\right) \cdot dn. \tag{A.11}
 \end{aligned}$$

is valid when $N \gg 1$. (Compare (A.1) and (A.9).) Note, when the above width

$$n = W_{\text{width}} = \pm \sqrt{\frac{N}{2}}, \tag{A.12}$$

the exponential falls off to $\exp(-1) \approx 0.37$ of its maximum value. (The maximum occurs when $n = 0$.) Henceforth, we shall call W_{width} the half-width of the distribution function.

To an untutored eye, the estimated size of the half-width, i.e., $\sqrt{(N/2)}$, would seem to be inordinately large. To alleviate such concerns all we need to remember is that the full distribution, in principle, can extend from $p = 0$ all the way to $p = N$. (Recall that N is extremely large. Indeed, it is “almost infinite,” loosely speaking!) Therefore, a more meaningful measure of the width is the “relative width,” which we shall denote by the symbol ϖ_{rel} . Here

$$\begin{aligned}\varpi_{\text{rel}} &= \frac{\text{Twice the half width}}{\text{Full range over which the distribution could extend}} \\ &= \left(\frac{2 W_{\text{width}}}{N} \right) = \left(\frac{2}{N} \right)^{1/2}.\end{aligned}\tag{A.13}$$

For example, when $N \sim 10^{24}$, the width $\sim 10^{12}$ appears to be very large. Yet, the relative width, $\varpi_{\text{rel}} \sim 10^{-12}$, is extremely small.

Despite the finding that the distribution is not infinitely peaked at the desired concentration¹¹ but has a finite width, the above discussion shows that for large N the desired state is overwhelmingly probable.

A.3.7 Plot of the Gaussian Distribution

Because a picture is worth many words, appended above is a plot of the normalized Gaussian distribution, F_y , as a function of the variable y (Fig. A.1).

$$y = n \sqrt{\frac{2}{N}}.\tag{A.14}$$

That is,

$$F_y = \frac{\exp(-y^2)}{\sqrt{\pi}}.\tag{A.15}$$

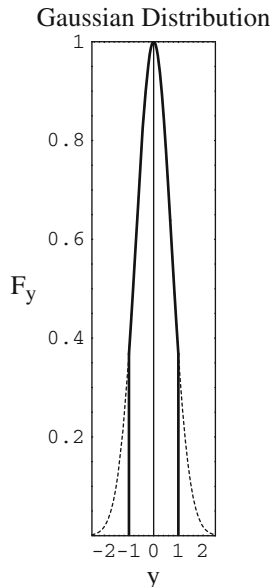
Note, the full area of the curve is normalized to unity, i.e.,

$$\int_{-\infty}^{+\infty} F_y dy = \int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{\sqrt{\pi}} dy = 1.\tag{A.16}$$

The two dark vertical lines, and the thick dark area of the curve, enclose that part of the distribution which lies within what we have called the width of the distribution.

¹¹Note: Here the desired concentration would have led to the mid-point $p = \frac{N}{2}$.

Fig. A.1 Gaussian Distribution Function



In terms of the abscissa y , these lines fall at positions $y = \pm 1$. It is interesting to note that this narrow region – consisting only of the width of the distribution – covers $\approx 84.3\%$ of the total weight of the distribution, i.e.,

$$\int_{-1}^{+1} F_y dy = 0.84271. \tag{A.17}$$

Indeed, if we extend this region to twice the width, that is $y = \pm 2$, we recover almost all, that is 99.53%, of the full weight of the distribution.

A.4 Moments of the Distribution Function: Remarks

Moments of appropriate distribution functions can often yield valuable information about thermodynamic states. To make use of this fact, in the following the so called normalized moments of the Gaussian distribution function are calculated. Next, the exact second normalized moment is calculated and is set to agree with the corresponding result of the Gaussian distribution function for general concentration.¹² It is interesting to note that for half-concentration, the Gaussian approximation – without any trying! – yields exact results for the second normalized moment.

¹²Recall that general concentration refers to the occupancy departing from the mid-point. This means that the probability that the i -th call on the PRNG returns an occupied site, i.e., $\sigma_i = 1$, is not necessarily equal to that which returns $\sigma_i = 0$.

A.5 Moments of the Gaussian Distribution Function

A.5.1 Un-Normalized Moments

The first several un-normalized moments of the Gaussian distribution function are calculated below. That is

$$I(a, n) = \left[\int_{-N/2}^{N/2} dx \exp(-ax^2) x^n dx \right]; \quad n = 0 \rightarrow 6 \text{ for } N \gg 1 \quad (\text{A.18})$$

A.5.1.1 Solution

It is clear that because of symmetry, $I(a, n)$ is zero for all odd values of n . To carry out the integrals for even n , consider doing the following:

$$\begin{aligned} I(a, 0) \cdot I(a, 0) &= \int_{-N/2}^{N/2} dx \exp(-ax^2) \int_{-N/2}^{N/2} dy \exp(-ay^2), \quad N \gg 1 \\ &= \int_{-N/2}^{N/2} \int_{-N/2}^{N/2} dx dy \exp[-a(x^2 + y^2)], \quad N \gg 1. \end{aligned} \quad (\text{A.19})$$

Changing over to polar coordinates, r, θ

$$x = r \cos \theta, \quad y = r \sin \theta,$$

and noting that

$$dx dy = \begin{vmatrix} \left(\frac{\partial x}{\partial r}\right)_\theta & \left(\frac{\partial x}{\partial \theta}\right)_r \\ \left(\frac{\partial y}{\partial r}\right)_\theta & \left(\frac{\partial y}{\partial \theta}\right)_r \end{vmatrix} dr d\theta = r dr d\theta,$$

the double integral over a square of size $N \times N$ in the Cartesian plane is transformed into one over a circular, planar disk of radius $N/2$.

$$\begin{aligned} [I(a, 0)]^2 &= \int_0^{2\pi} d\theta \int_0^{N/2} dr \exp(-ar^2) r, \quad N \gg 1 \\ &= 2\pi \left(\frac{1}{-2a}\right) \left[\exp\left\{-a\left(\frac{N}{2}\right)^2\right\} - 1 \right], \quad N \gg 1 \\ &\approx \pi/a. \end{aligned} \quad (\text{A.20})$$

Regarding the limits, we note that even though the square and the circle do not exactly fit over each other, for $N/2 \gg 1$ the discrepant region is so very far away from the origin that the exponential in the integral makes the discrepancy vanishingly small. Therefore, as long as a is positive, without any loss in accuracy, integrals $I(a, n)$ can be evaluated by replacing N by ∞ . Consequently the following result is close to being exact.

$$I(a, 0) = \sqrt{\frac{\pi}{a}}. \quad (\text{A.21})$$

For $n > 0$, the n -th moment $I(a, n)$ can be evaluated by repeated differentiation with respect to a . For instance, the second and the fourth moments of the Gaussian distribution, $\exp(-ax^2)$, are:

$$I(a, 2) = -\frac{dI(a, 0)}{da} = \int_{-\infty}^{\infty} dx \exp(-ax^2)x^2 = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}. \quad (\text{A.22})$$

$$\begin{aligned} I(a, 4) &= -\frac{dI(a, 2)}{da} = \int_{-\infty}^{\infty} dx \exp(-ax^2)x^4 = \frac{1}{2} \cdot \frac{3}{2} \cdot \sqrt{\frac{\pi}{a^5}}; \\ I(a, 6) &= -\frac{dI(a, 4)}{da} = \int_{-\infty}^{\infty} dx \exp(-ax^2)x^6 \\ &= \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2} \cdot \sqrt{\frac{\pi}{a^7}} \end{aligned} \quad (\text{A.23})$$

A.5.2 Normalized Moments of the Gaussian Distribution Function

Let us define the j -th normalized Gaussian moment for general choice of the parameter a as follows:

$$\Delta_j^G(a) = \frac{I(a, j)}{I(a, 0)}. \quad (\text{A.24})$$

Clearly, by definition, the 0-th normalized moment, $\Delta_0^G(a)$, is unity. And the other normalized Gaussian moments are:

$$\Delta_2^G(a) = \left(\frac{1}{2a}\right); \Delta_4^G(a) = \left(\frac{3}{4a^2}\right); \Delta_6^G(a) = \left(\frac{15}{8a^3}\right). \quad (\text{A.25})$$

A.5.2.1 Normalized Moments of the Gaussian Distribution Function for Half Occupancy

It is interesting to record the normalized moments for the Gaussian distribution that obtain in the region around half-concentration. The relevant equation – i.e., (A.11) – tells us that, for half-concentration, in (A.25) the parameter a has to be replaced by $\frac{2}{N}$. As a result one has:

$$a \equiv a_\mu; a_{\frac{1}{2}} = \left(\frac{2}{N} \right), \quad (\text{A.26})$$

$$\Delta_2^G \left(a_{\frac{1}{2}} \right) = \left(\frac{N}{4} \right) = \left(\frac{1}{2a_{\frac{1}{2}}} \right), \quad (\text{A.27})$$

$$\Delta_4^G \left(a_{\frac{1}{2}} \right) = \left(\frac{3 N^2}{16} \right) = \left(\frac{3}{4a_{\frac{1}{2}}^2} \right), \quad (\text{A.28})$$

$$\Delta_6^G \left(a_{\frac{1}{2}} \right) = \left(\frac{15 N^3}{64} \right) = \left(\frac{15}{8a_{\frac{1}{2}}^3} \right). \quad (\text{A.29})$$

Note: As indicated in (A.40) below, for general concentration, that is for $1 > \mu > 0$, the appropriate choice for the variable a_μ is: $a_\mu \equiv \left[\frac{1}{2N\mu(1-\mu)} \right]$.

A.5.3 Normalized Moments of the Exact Distribution Function for General Occupancy

The overall average value of the occupancy variable σ_i , written as $\langle \sigma_i \rangle$, is equal to the concentration μ of the occupied sites for which $\sigma_i = 1$. Note the unoccupied sites, for which $\sigma_i = 0$ and whose concentration is $(1 - \mu)$, contribute nothing to $\langle \sigma_i \rangle$. Thus,

$$\langle \sigma_i \rangle = \mu \times 1 + (1 - \mu) \times 0 = \mu, \quad (\text{A.30})$$

where

$$1 \geq \mu \geq 0. \quad (\text{A.31})$$

The present notation for μ is the same as originally used in (A.2).

For the exact distribution, a convenient formal representation for the n -th normalized moment, $\Delta_n^{\text{exact}}(\mu)$, is the following:

$$\Delta_n^{\text{exact}}(\mu) = \langle \left[\sum_{i=1}^N (\sigma_i - \mu) \right]^n \rangle. \quad (\text{A.32})$$

As shown below, the zeroth order normalized moment, $\Delta_0^{\text{exact}}(\mu)$, is unity. Similarly, because of the requirement that the thermodynamic average of σ_i – to be denoted as $\langle \sigma_i \rangle$ – be equal to the density μ of the occupied sites, the first moment $\Delta_1^{\text{exact}}(\mu)$ is equal to zero.

$$\begin{aligned}\Delta_0^{\text{exact}}(\mu) &= \langle [\Sigma_i^N (\sigma_i - \mu)]^{n=0} \rangle \\ &= \langle 1 \rangle = 1; \\ \Delta_1^{\text{exact}}(\mu) &= \langle [\Sigma_i^N (\sigma_i - \mu)]^{n=1} \rangle \\ &= \langle \Sigma_i^N \sigma_i \rangle - \langle N\mu \rangle \\ &= \Sigma_i^N \langle \sigma_i \rangle - N\mu = \Sigma_i^N \mu - N\mu = 0.\end{aligned}\tag{A.33}$$

A.5.4 Exact, Second Normalized Moment

In order to calculate

$$\Delta_2^{\text{exact}}(\mu) = \langle [\Sigma_i^N (\sigma_i - \mu)]^2 \rangle,\tag{A.34}$$

expand the square, and note that i is a dummy index. Therefore

$$\begin{aligned}\Delta_2^{\text{exact}}(\mu) &= \langle \Sigma_i^N (\sigma_i - \mu) \cdot \Sigma_j^N (\sigma_j - \mu) \rangle \\ &= \langle \Sigma_i^N \Sigma_j^N (\sigma_i \sigma_j) \rangle \\ &\quad - N\mu [\Sigma_i^N \langle \sigma_i \rangle + \Sigma_j^N \langle \sigma_j \rangle] + N^2 \mu^2.\end{aligned}\tag{A.35}$$

Because

$$\Sigma_i^N \langle \sigma_i \rangle = \Sigma_j^N \langle \sigma_j \rangle = \Sigma_i^N \mu = N\mu,\tag{A.36}$$

the only term that remains to be evaluated is:

$$\begin{aligned}\gamma_2 &= \langle \Sigma_i^N \Sigma_j^N \sigma_i \sigma_j \rangle \\ &= \Sigma_i^N \Sigma_{j \neq i}^N \langle \sigma_i \sigma_j \rangle + [\Sigma_i^N \langle \sigma_i \sigma_j \rangle (j = i)] \\ &= \Sigma_i^N \Sigma_{j \neq i}^N \langle \sigma_i \sigma_j \rangle + [\Sigma_i^N \langle (\sigma_i)^2 \rangle].\end{aligned}\tag{A.37}$$

Because σ_i can take on only the two possible values 1 and 0, therefore,

$$(\sigma_i)^2 = \sigma_i.$$

This property will be invoked and also use will be made of the fact that any two independent calls to the perfect random number are completely uncorrelated. In other words,

$$\langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle = \mu^2, \text{ for } j \neq i.$$

Therefore, (A.37) becomes

$$\begin{aligned} \gamma_2 &= \sum_i^N \sum_{j \neq i}^N \langle \sigma_i \rangle \langle \sigma_j \rangle + \sum_i^N \langle \sigma_i \rangle^2 \\ &= \sum_i^N \sum_{j \neq i}^N \mu^2 + \sum_i^N \mu^2 \\ &= N(N-1)\mu^2 + N\mu^2. \end{aligned} \quad (\text{A.38})$$

Equations (A.38), (A.37), (A.36) and (A.32) lead to the following exact result for the second order normalized frequency moment:

$$\begin{aligned} \Delta_2^{\text{exact}}(\mu) &= \gamma_2 - N\mu(N\mu + N\mu) + N^2\mu^2 \\ &= N\mu - N\mu^2 = N\mu(1 - \mu). \end{aligned} \quad (\text{A.39})$$

Note, for half-concentration $\Delta_2^{\text{exact}}(\mu = \frac{1}{2})$, as confirmed by the right hand side of (A.39), is equal to $N/4$. This result is identical to that given by the Gaussian approximation: $\Delta_2^G(a_{\frac{1}{2}})$. [See (A.27).] Clearly, therefore, for general concentration, μ , (A.39) suggests that, in view of (A.27), the dependence of the variable a_μ on μ should be as follows:

$$\left(\frac{1}{2a_\mu} \right) = \Delta_2^{\text{exact}}(\mu) = N\mu(1 - \mu). \quad (\text{A.40})$$

Consequently, the Gaussian approximation yields exact result for the second order normalized moment. This holds true not only for half-concentration, $\mu = \frac{1}{2}$, but also for general (concentration) μ . That is

$$\Delta_2^G(a_\mu) = \Delta_2^{\text{exact}}(\mu). \quad (\text{A.41})$$

Indeed, as will be shown later, with $a_\mu = \left(\frac{1}{2N\mu(1-\mu)} \right)$, the Gaussian approximation yields results for the normalized moments that are exact to the leading order in $\left(\frac{1}{N} \right)$.

A.5.5 *Exact, Third → Sixth Normalized Moments*

For brevity, only the essential steps will be given below.

The third order normalized moment is:

$$\Delta_3^{\text{exact}}(\mu) = \langle [\sum_i^N (\sigma_i - \mu)]^3 \rangle = \gamma_3 - 3\mu N\gamma_2 + 2(\mu N)^3, \quad (\text{A.42})$$

where γ_2 is as given in (A.37) and

$$\begin{aligned}\gamma_3 &= \sum_i^N \sum_j^N \sum_k^N \langle \sigma_i \sigma_j \sigma_k \rangle \\ &= N(N-1)(N-2)\mu^3 + 3N(N-1)\mu^2 + N\mu.\end{aligned}\quad (\text{A.43})$$

Thus the exact result for the third order normalized moment for the general concentration is the following:

$$\Delta_3^{\text{exact}}(\mu) = N\mu(1 - 3\mu + 2\mu^2).\quad (\text{A.44})$$

Note, when the concentration μ of occupied sites is $\frac{1}{2}$ – i.e., the half concentration case – the third moment, like all the odd-order moments, is equal to zero.

A.5.6 Exercise: III

Using the procedure described for calculating γ_2 , derive (A.43). (See (A.37) and (A.38)) Indeed, a sufficiently motivated student may even want to derive (A.45), (A.47) and (A.48) that are given below.

A.5.7 The Fourth Moment

In addition to γ_2 and γ_3 , the evaluation of the fourth moment also requires the knowledge of γ_4 .

$$\begin{aligned}\gamma_4 &= \sum_i^N \sum_j^N \sum_k^N \sum_l^N \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle \\ &= N(N-1)(N-2)(N-3)\mu^4 + 6N(N-1)(N-2)\mu^3 \\ &\quad + 7N(N-1)\mu^2 + N\mu.\end{aligned}\quad (\text{A.45})$$

Combination of this with the results of the averages of the two- and three-site sums, γ_2 and γ_3 , leads to the following exact result for the fourth moment.

$$\begin{aligned}\Delta_4^{\text{exact}}(\mu) &= \gamma_4 - 4\mu N\gamma_3 + 6\mu^2 N^2 \gamma_2 - 3\mu^4 N^4 \\ &= 3N^2 \mu^2 (1 - \mu)^2 + N\mu(1 - 7\mu + 12\mu^2 - 6\mu^3).\end{aligned}\quad (\text{A.46})$$

While the procedure for calculating the higher order moments is similar, the effort involved rapidly increases with the rise of the order.

A.5.8 Calculation of the Fifth and the Sixth Normalized Moments

With somewhat more than the usual amount of effort one finds:

$$\begin{aligned}
 \gamma_5 &= \sum_i^N \sum_j^N \sum_k^N \sum_l^N \sum_m^N \langle \sigma_i \sigma_j \sigma_k \sigma_l \sigma_m \rangle \\
 &= N(N-1)(N-2)(N-3)(N-4)\mu^5 \\
 &\quad + 10N(N-1)(N-2)(N-3)\mu^4 \\
 &\quad + 25N(N-1)(N-2)\mu^3 + 15N(N-1)\mu^2 + N\mu \quad (\text{A.47})
 \end{aligned}$$

and

$$\begin{aligned}
 \gamma_6 &= \sum_i^N \sum_j^N \sum_k^N \sum_l^N \sum_m^N \sum_n^N \langle \sigma_i \sigma_j \sigma_k \sigma_l \sigma_m \sigma_n \rangle \\
 &= N(N-1)(N-2)(N-3)(N-4)(N-5)\mu^6 \\
 &\quad + 15N(N-1)(N-2)(N-3)(N-4)\mu^5 \\
 &\quad + 65N(N-1)(N-2)(N-3)\mu^4 + 90N(N-1)(N-2)\mu^3 \\
 &\quad + 31N(N-1)\mu^2 + N\mu. \quad (\text{A.48})
 \end{aligned}$$

The rest of the task is easy. We have

$$\begin{aligned}
 \Delta_5^{\text{exact}}(\mu) &= (\gamma_5 - 5N\mu\gamma_4 + 10N^2\mu^2\gamma_3) \\
 &\quad - (10N^3\mu^3\gamma_2 + 4N^5\mu^5) \\
 &= 10N^2\mu^2(1 - 4\mu + 5\mu^2 - 2\mu^3) \\
 &\quad + N\mu(1 - 15\mu + 50\mu^2 - 60\mu^3 + 24\mu^4) \quad (\text{A.49})
 \end{aligned}$$

and

$$\begin{aligned}
 \Delta_6^{\text{exact}}(\mu) &= (\gamma_6 - 6N\mu\gamma_5 + 15N^2\mu^2\gamma_4) \\
 &\quad - (20N^3\mu^3\gamma_3 + 15N^4\mu^4\gamma_2 - 5N^6\mu^6) \\
 &= 15\mu^3N^3(1 - 3\mu + 3\mu^2 - \mu^3) \\
 &\quad + 5N^2\mu^2(5 - 36\mu + 83\mu^2 - 78\mu^3 + 26\mu^4) \\
 &\quad + N\mu(1 - 31\mu + 180\mu^2 - 390\mu^3 + 360\mu^4 - 120\mu^5). \quad (\text{A.50})
 \end{aligned}$$

For the normalized moments, it is instructive to compare the exact results with those given by the corresponding Gaussian approximation. Remember that the appropriate choice for the parameter a_μ – that is to be used instead of a in the Gaussian expansion valid for general concentration of occupied sites – is as recorded in

(A.40). Consequently, one has

$$\begin{aligned} \left[\frac{\Delta_2^G(a_\mu)}{N^{2/2}} \right] &= \left[\frac{\Delta_2^{\text{exact}}(\mu)}{N^{2/2}} \right] = \left[\frac{\left(\frac{1}{2a_\mu} \right)}{N^{2/2}} \right] = \mu(1 - \mu); \\ \left[\frac{\Delta_4^G(a_\mu)}{N^{4/2}} \right] &= \left[\frac{\left(\frac{3}{4a_\mu^2} \right)}{N^{4/2}} \right] = 3\mu^2(1 - \mu)^2, \\ \left[\frac{\Delta_4^{\text{exact}}(\mu)}{N^{4/2}} \right] &= \left[\frac{\Delta_4^G(a_\mu)}{N^{4/2}} \right] + \left[\frac{\mu(1 - 7\mu + 12\mu^2 - 6\mu^3)}{N} \right]; \\ \left[\frac{\Delta_6^G(a_\mu)}{N^{6/2}} \right] &= \left[\frac{\left(\frac{15}{8a_\mu^3} \right)}{N^{6/2}} \right] = 15\mu^3(1 - \mu)^3, \\ \left[\frac{\Delta_6^{\text{exact}}(\mu)}{N^{6/2}} \right] &= \left[\frac{\Delta_6^G(a_\mu)}{N^{6/2}} \right] + \left[\frac{5\mu^2(5 - 36\mu + 83\mu^2 - 78\mu^3 + 26\mu^4)}{N} \right] \\ &\quad + \left(\frac{\mu}{N^2} \right) [1 - 31\mu + 180\mu^2 - 390\mu^3 + 360\mu^4 - 120\mu^5]. \quad (\text{A.51}) \end{aligned}$$

$$\begin{aligned} \left[\frac{\Delta_3^G(a_\mu)}{N^{3/2}} \right] &= 0, \\ \left[\frac{\Delta_3^{\text{exact}}(\mu)}{N^{3/2}} \right] &= \left[\frac{\Delta_3^G(a_\mu)}{N^{3/2}} \right] + \mu \left[\frac{(1 - 3\mu + 2\mu^2)}{N^{1/2}} \right]; \\ \left[\frac{\Delta_5^G(a_\mu)}{N^{5/2}} \right] &= 0, \\ \left[\frac{\Delta_5^{\text{exact}}(\mu)}{N^{5/2}} \right] &= \left[\frac{\Delta_5^G(a_\mu)}{N^{5/2}} \right] + 10\mu^2 \left[\frac{(1 - 4\mu + 5\mu^2 - 2\mu^3)}{N^{1/2}} \right] \\ &\quad + \mu \left[\frac{(1 - 15\mu + 50\mu^2 - 60\mu^3 + 24\mu^4)}{N^{3/2}} \right]. \quad (\text{A.52}) \end{aligned}$$

(Note: For $\mu = \frac{1}{2}$, odd-order moments are vanishing.)

As mentioned before, while the second moment is exactly given by the Gaussian approximation, the third, fourth, fifth and the sixth moments are “exact” only to the leading order in the large N limit. Because in thermodynamic systems N is extraordinarily large, the Gaussian approximation is impressively accurate.

A.5.9 Concluding Remark

For $\mu = 1$ or 0 , all exact, normalized, moments are vanishing. Also, despite the fact that the Gaussian approximation – which is symmetric – cannot be expected to be accurate over the whole concentration range, in the immediate vicinity of the most probable state the exact distribution function appears to be very nearly symmetric and is close to being a Gaussian. This is testified to by the following facts:

1. The Gaussian approximation exactly reproduces the – zeroth and the – second moment of the distribution.
2. The approximation predicts that the ratio of the fourth normalized moment to the square of the second normalized moment is equal to 3 for general values of μ . That is,

$$\frac{\Delta_4^G(a_\mu)}{[\Delta_2^G(a_\mu)]^2} = 3. \quad (\text{A.53})$$

The same is also true, to the leading order in N , for the exact moments: that is,

$$\frac{\Delta_4^{\text{exact}}(\mu)}{[\Delta_2^{\text{exact}}(\mu)]^2} = 3 + (N^{-1}) \left[\frac{1}{\mu(1-\mu)} \right]^2 [1 - 7\mu + 12\mu^2 - 6\mu^3]. \quad (\text{A.54})$$

3. The Gaussian approximation predicts that the ratio of the sixth normalized moment to the cube of the second normalized moment is equal to 15 for general values of μ . That is,

$$\frac{\Delta_6^G(a_\mu)}{[\Delta_2^G(a_\mu)]^3} = 15. \quad (\text{A.55})$$

The same is also true, to the leading order in N , for the exact moments: i.e.,

$$\frac{\Delta_6^{\text{exact}}(\mu)}{[\Delta_2^{\text{exact}}(\mu)]^3} = 15 + (N^{-1}) \left[\frac{5\mu^2(5 - 36\mu + 83\mu^2 - 78\mu^3 + 26\mu^4)}{\mu^3(1-\mu)^3} \right] + O(N^{-2}). \quad (\text{A.56})$$

4. While the Gaussian distribution is symmetric and thus leads to vanishing odd-order normalized moments, the exact distribution is asymmetric and its odd-order normalized moments are non-vanishing. Such asymmetry is very small in the neighborhood of the most probable state. This is demonstrated by the size of the normalized third- and fifth-order moments for very large N . Here, instead of $\Delta_3^{\text{exact}}(\mu)$ and $\Delta_5^{\text{exact}}(\mu)$ having the usual, canonical size, namely

$$[\Delta_n^{\text{exact}}(\mu)]^{1/n} \rightarrow O(N^{1/2}), n = 2, 3, \dots \quad (\text{A.57})$$

their size is actually much smaller, i.e.,

$$[\Delta_3^{\text{exact}}(\mu)]^{1/3} \rightarrow O(N^{1/3}), \quad (\text{A.58})$$

and

$$[\Delta_5^{\text{exact}}(\mu)]^{1/5} \rightarrow O(N^{2/5}). \quad (\text{A.59})$$

Thus, as long as a is chosen to be equal to $a_\mu = \frac{1}{2N\mu(1-\mu)}$, the line-shape, $\exp(-a_\mu z^2)$, retains its physical validity for large N . Another feature to note is the size of the relative fluctuation¹³ as a function of the concentration μ .

$$\varpi_{\text{rel}} = \sqrt{2\Delta_2^{\text{exact}}(\mu)/(N\mu)} = \sqrt{2(1-\mu)/(N\mu)}. \quad (\text{A.60})$$

Not unexpectedly when μ approaches unity, almost all the calls to the random number generator return the value 1. And, additionally the total number of *occupied* sites becomes large, approaching N . Thus the relative width of the distribution narrows still further. Opposite is the case when μ approaches zero because now there may be some calls to the generator that actually return the value unity while the average of the total number of occupied sites, $N\mu$, has become very small. This fact merely re-states the obvious: the relative fluctuation in a small sample is large.

A.5.10 Summary

In a macroscopically large system, the most probable configuration is overwhelmingly so. Therefore, the result of any “macroscopic” measurement is well described by an accurate calculation of the most probable state.

¹³Compare (A.13).

Appendix B

Perfect Gas Revisited

As mentioned before, a perfect gas consists of N identical molecules, each of the same mass. The number of molecules is very large: that is, $N \gg 1$. The gas is enclosed in a vessel of arbitrary shape. The volume of the vessel is V . There are no intermolecular interactions, the size of the molecules is vanishingly small, the containing walls of the vessel are smooth and featureless. All collisions between the molecules and the walls are perfectly elastic; effects of gravity are absent; no other external forces are present. Further, the molecules are in a state of random motion.

Here, in this appendix, we first revisit the standard thermodynamics treatment for a qualitative derivation of the equation of state. This time, somewhat greater detail is provided than was done previously. Next we use an elementary statistical mechanical procedure, that employs Boltzmann–Maxwell–Gibbs distribution, to precisely and quantitatively derive the equation of state.

B.1 Monatomic Perfect Gas

All the molecules are monatomic and each has mass m . The molecules – meaning the atoms – are all of zero size and in three dimensions each has only three possible degrees of freedom related to its translational motion. The atomic size being zero forbids any meaningful possibility of self rotation. Furthermore, zero interatomic interaction disallows any interparticle coupling.

B.1.1 Pressure

Consider a vessel of arbitrary shape. The walls of the vessel are smooth and their shape can be represented in terms of non-singular equations. Consider a small but finite volume of gas inside the vessel. For simplicity, assume that the small volume

is shaped as a parallelepiped whose three, mutually perpendicular, imaginary-walls¹ lie along the x , y , z axes of a Cartesian coordinate system and are of length Δx , Δy , and Δz . Assume the number of molecules, N_{pp} , within such a parallelepiped is large compared with unity, i.e., $N \gg N_{pp} \gg 1$.

Set the origin of the Cartesian coordinates at the bottom left-hand corner of the parallelepiped and the positive direction of the axes along the three edges. As such, the top corner diagonally opposite to the origin is at the point $(\Delta x, \Delta y, \Delta z)$.

Examine the course of events involved in molecular collisions against the two walls of the parallelepiped that are perpendicular to the x -axis. Denote the x -component of the velocity of the i -th molecule – $i = 1, 2, \dots, N_{pp}$ – as $v_{i,x}$.

Perfect elasticity of collisions requires that upon striking the right-hand side wall – at $x = (+\Delta x)$ – with x component of momentum $m \cdot v_{i,x}$ the molecule gets reflected and the x component of its momentum becomes $-m \cdot v_{i,x}$. Accordingly, the change in x component of momentum of the molecule after one collision is:

$$\begin{aligned} & \text{final momentum of colliding molecule} - \text{its initial momentum} \\ &= [-m \cdot v_{i,x}] - [m \cdot v_{i,x}] = -2m \cdot v_{i,x}. \end{aligned} \quad (\text{B.1})$$

Because there are no external forces, the total momentum in any direction is conserved. Invoking this fact for the x -direction leads to the requirement:

$$\begin{aligned} & \text{change in total momentum} \\ &= \text{change in particle momentum} + \text{change in momentum of wall} \\ &= -2m \cdot v_{i,x} + \delta(\text{mom wall})_{i,x} = 0. \end{aligned} \quad (\text{B.2})$$

That is, a single collision of the wall perpendicular to the x -axis causes an increase in the x -component of the momentum of the wall equal to

$$\Delta(\text{mom wall})_{i,x} = 2m \cdot v_{i,x}. \quad (\text{B.3})$$

The absence of slowing down mechanisms insures that after traversing across the parallelepiped to the left-hand side wall placed at $x = 0$ this molecule returns for another collision against the original wall at $x = +\Delta x$. Such a round-trip – from the right-hand side wall to the wall on the left and then back to the wall on the right – is of length $2 \Delta x$. Further, it is traversed at constant speed $|v_{i,x}|$. Therefore,

¹Although we have called the walls imaginary, we do not treat them as representing an open boundary. Indeed, it is not unreasonable to impose boundary conditions on these “imaginary” walls which are more restrictive than the conditions for an open boundary. For instance, the passage of a sufficiently long interval of time ensures that equal number of particles with roughly the same energy have been incident from opposite directions on a given “imaginary wall.” This behavior is not unlike that which results from specular boundary conditions and results in collisions that can be treated as being perfectly elastic.

the time, Δt , taken by the molecule for the round trip travel is

$$\Delta t = \frac{\text{Distance Traveled}}{\text{Speed of Travel}} = \frac{2 \Delta x}{|v_{i,x}|}. \quad (\text{B.4})$$

As a result, the rate of transfer of momentum by one molecule to this wall,

[momentum transferred in one collision/time taken between the collisions],

can be written as

$$\frac{\Delta(\text{mom wall})_{i,x}}{\Delta t} = \frac{2m \cdot |v_{i,x}|}{\{2\Delta x/|v_{i,x}|\}} = \left(\frac{m}{\Delta x}\right) v_{i,x}^2. \quad (\text{B.5})$$

Summing this over all the molecules— that is for $i = 1 \rightarrow N_{\text{pp}}$ — within the parallelepiped gives us the total transfer rate of momentum to the right hand side wall. According to Newton's second law of motion, this is equal to the force, F_{pp} , exerted by the gas on the relevant wall of the parallelepiped.

$$F_{\text{pp}} = \sum_{i=1}^{N_{\text{pp}}} \frac{\Delta(\text{mom wall})_{i,x}}{\Delta t} = \left(\frac{m}{\Delta x}\right) \sum_{i=1}^{N_{\text{pp}}} v_{i,x}^2. \quad (\text{B.6})$$

The force F_{pp} acts normal to the wall under examination. Accordingly, it exerts pressure P_{pp} , which is defined as the perpendicular force on the wall per unit area,

$$P_{\text{pp}} = F_{\text{pp}}/(\text{Area of the Wall}) = \frac{F_{\text{pp}}}{\Delta y \Delta z}. \quad (\text{B.7})$$

Combining this with (B.6) yields

$$\begin{aligned} P_{\text{pp}} &= \left(\frac{m}{\Delta x \Delta y \Delta z}\right) \sum_i^{N_{\text{pp}}} v_{i,x}^2 \\ &= \left(\frac{m}{V_{\text{pp}}}\right) \sum_i^{N_{\text{pp}}} v_{i,x}^2 = \left(\frac{m}{V_{\text{pp}}}\right) N_{\text{pp}} \langle v_x^2 \rangle_{\text{pp}}. \end{aligned} \quad (\text{B.8})$$

Here, $V_{\text{pp}} = (\Delta x \Delta y \Delta z)$ is the volume of the elementary². parallelepiped under consideration and the pointed brackets with suffix pp , i.e., $\langle v_x^2 \rangle_{\text{pp}}$ signify an average, of $v_{i,x}^2$, over all — i.e., for $i = 1, \dots, N_{\text{pp}}$ — molecules in the parallelepiped.

$$\langle v_x^2 \rangle_{\text{pp}} = \frac{\sum_i^{N_{\text{pp}}} v_{i,x}^2}{N_{\text{pp}}}. \quad (\text{B.9})$$

²Yet macroscopic, because $N_{\text{pp}} \gg 1$.

The gas is isotropic. Therefore,

$$\begin{aligned} \langle v_x^2 \rangle_{pp} = \langle v_y^2 \rangle_{pp} = \langle v_z^2 \rangle_{pp} &= \frac{1}{3} \left[\langle v_x^2 \rangle_{pp} + \langle v_y^2 \rangle_{pp} + \langle v_z^2 \rangle_{pp} \right] \\ &= \frac{1}{3} \langle \mathbf{v}^2 \rangle_{pp}. \end{aligned} \quad (\text{B.10})$$

Thus, (B.8) can be re-cast as

$$P_{pp} V_{pp} = m N_{pp} \langle v_x^2 \rangle_{pp} = \frac{m}{3} N_{pp} \langle \mathbf{v}^2 \rangle_{pp}. \quad (\text{B.11})$$

In the above equation all the three quantities V_{pp} , N_{pp} and $\langle \mathbf{v}^2 \rangle_{pp}$ are independent of the direction x , y or z . Therefore, the pressure P_{pp} is also independent of the direction.

Now sum the above equation over all the parallelepipeds designated by the index pp – or equivalently, over all the molecules – in the vessel.

$$\sum_{\text{all } pp} P_{pp} V_{pp} = \left(\frac{m}{3} \right) \sum_{\text{all } pp} N_{pp} \langle \mathbf{v}^2 \rangle_{pp} = \left(\frac{m}{3} \right) N \langle \mathbf{v}^2 \rangle. \quad (\text{B.12})$$

In the above, the pointed brackets without any suffix, e.g., $\langle \mathbf{v}^2 \rangle$, represent an average over all the N molecules. That is

$$\langle \mathbf{v}^2 \rangle = \sum_{\text{all } pp} \frac{N_{pp} \langle \mathbf{v}^2 \rangle_{pp}}{N}. \quad (\text{B.13})$$

Define the pressure P inside the vessel from the relationship

$$\sum_{\text{all } pp} P_{pp} V_{pp} = PV. \quad (\text{B.14})$$

Given that the surface enclosing the container does not possess pathological singularities, the sum $\sum_{\text{all } pp}$ over a very large number of appropriately small parallelepipeds of volumes V_{pp} reproduces the actual volume V that encloses the container. That is,

$$\sum_{\text{all } pp} V_{pp} = V.$$

Multiplying both sides by the constant P gives

$$P \sum_{\text{all } pp} V_{pp} = \sum_{\text{all } pp} P V_{pp} = PV. \quad (\text{B.15})$$

Subtraction of (B.14) from (B.15) leads to the equality:

$$\sum_{\text{all pp}} (P - P_{\text{pp}}) V_{\text{pp}} = 0. \quad (\text{B.16})$$

The above sum is over an arbitrary number of different parallelepipeds whose volumes sum to the total volume V . Because these volumes, V_{pp} , are all arbitrary—other than each being very small but still containing a moderate number of molecules – therefore, the above equation can be satisfied only if

$$P_{\text{pp}} = P \quad (\text{B.17})$$

for all parallelepipeds. This result is in agreement with that implicit in Pascal’s law, which asserts that the pressure is constant throughout the vessel. Note also that (B.12) and (B.14) lead to an important relationship

$$PV = \left(\frac{m}{3}\right) N \langle v^2 \rangle. \quad (\text{B.18})$$

B.1.2 Classical Statistics: Boltzmann–Maxwell–Gibbs Distribution

Consider a three-dimensional system of N atoms whose total volume is equal to V . The location and momentum of an infinitesimal sized atom “ i ,” is specified by 3 position co-ordinates, e.g., $q_{i,x}, q_{i,y}, q_{i,z}$, and 3 vector-components, e.g., $p_{i,x}, p_{i,y}, p_{i,z}$, of the momentum \vec{p}_i . Denote the 3- N position co-ordinates of the N atoms as $= Q$, the 3- N components of the momentum vectors divided by h^{3N} as $= P$, and use the notation

$$\begin{aligned} dQ &= dq_{1,x} dq_{1,y} dq_{1,z} \dots dq_{N,x} dq_{N,y} dq_{N,z}, \\ dP &= dp_{1,x} dp_{1,y} dp_{1,z} \dots dp_{N,x} dp_{N,y} dp_{N,z} / (h^{3N}). \end{aligned} \quad (\text{B.19})$$

Next, define the BMG distribution factor $f(Q, P)$.

$$f(Q, P) = \frac{\exp(-\beta\mathcal{H})}{\int_Q \dots \int_P \exp(-\beta\mathcal{H}) \cdot dQ \cdot dP}. \quad (\text{B.20})$$

Here

$$\beta = \frac{1}{k_{\text{B}}T} = \left(\frac{N_{\text{A}}}{RT}\right) = \left(\frac{N}{nRT}\right), \quad (\text{B.21})$$

\mathcal{H} is the Hamiltonian – i.e., the functional form of the system energy in terms of the $6N$ variables Q and P – and T represents the statistical-mechanical temperature – usually called the Kelvin temperature and labeled as K . Constants n and N_A have already been defined in (2.12). Additionally, k_B , and therefore R , are also constants. That is,

$$\begin{aligned} R &= 8.3144\ 72(15)\ \text{J mol}^{-1}\text{K}^{-1}, \\ k_B &= 1.38065\ 04(24) \times 10^{-23}\ \text{JK}^{-1}. \end{aligned} \quad (\text{B.22})$$

R is called the “molar gas constant” and k_B is known as the Boltzmann constant.

In accordance with the Boltzmann–Maxwell–Gibbs (BMG) postulates in thermodynamic equilibrium the normalized average (i.e., the observed value $\langle \Omega \rangle$) of any thermodynamic function, $\Omega(Q, P)$, is given by the following integral³

$$\langle \Omega \rangle = \int_Q \dots \int_P [\Omega(Q, P)] \cdot f(Q, P) \cdot dQ \cdot dP. \quad (\text{B.23})$$

Note, $f(Q, P)$ here is the same as defined in (B.20). Further, that the integrations over the $3N$ position variables, Q , occur over the maximum (three dimensional) volume V available to each and all of the N atoms. The integration over the $3N$ momentum variables is over the infinite range from $-\infty \rightarrow +\infty$.

The denominator that appears in (B.20), i.e.,

$$\int_Q \dots \int_P \exp(-\beta\mathcal{H}) \cdot dQ \cdot dP, \quad (\text{B.24})$$

is of great importance. (Remember $\beta = \frac{1}{k_B T}$.) Except for a multiplying constant, this denominator is proportional to the so-called “Partition Function,” $\Xi(N, V, T)$, which will be described in detail later. The partition function is fundamental to the use of statistical mechanics. We shall have occasion to expand on this statement in the chapter titled “Statistical-Thermodynamics.”

Because for a perfect gas inter-atomic interaction is assumed to be completely absent, the Hamiltonian \mathcal{H} in (B.20), (B.23), and (B.24) contains only the kinetic energy and depends on just the momenta of the N monatoms,⁴ i.e.,

$$\mathcal{H} = \frac{1}{2m} \sum_{j=1}^N \left(p_{j,x}^2 + p_{j,y}^2 + p_{j,z}^2 \right). \quad (\text{B.25})$$

³Note that normalized average of any constant, say α , is equal to itself: that is, $\langle \alpha \rangle = \alpha$.

⁴Diatomic Perfect Gas is treated in Chap. 11.

B.1.3 Energy in a Monatomic Perfect Gas

According to (B.25), the average value of the energy – here to be called the internal energy and denoted as U – in a monatomic perfect gas of N , non-interacting infinitesimal sized atoms each of mass m , is given by the relation

$$\langle \mathcal{H} \rangle = \frac{1}{2m} \sum_{j=1}^N \left[\langle (p_{j,x}^2) \rangle + \langle (p_{j,y}^2) \rangle + \langle (p_{j,z}^2) \rangle \right]. \quad (\text{B.26})$$

Because there are no direction dependent forces⁵ present, the gas is isotropic. Therefore, the above can be written as

$$\langle \mathcal{H} \rangle = \frac{1}{2m} \sum_{j=1}^N \left[3 \langle (p_{j,x}^2) \rangle \right] = \sum_{j=1}^N \frac{\langle \mathbf{p}_j^2 \rangle}{2m}. \quad (\text{B.27})$$

Let us now use the BMG procedure, given in (B.20), (B.23), and (B.24), and calculate the thermodynamic average $\langle (p_{i,x}^2) \rangle$ for any arbitrary atom i .

$$\langle (p_{i,x}^2) \rangle = \frac{\int_Q \cdots \int_P \cdots [p_{i,x}^2] \cdot \exp(-\beta\mathcal{H}) \cdot dQ \cdot dP}{\int_Q \cdots \int_P \cdots \exp(-\beta\mathcal{H}) \cdot dQ \cdot dP}. \quad (\text{B.28})$$

In the above equation, the integral over Q is trivial because \mathcal{H} as well as $p_{i,x}^2$ do not depend on any of the $3N$ position coordinates: $Q = \dots, q_{i,x}, q_{i,y}, q_{i,z}, \dots, etc.$ Therefore, each of the N atoms simply contributes a factor V equal to the maximum volume available to it. That is, for any atom j , we have

$$\int_Q \cdots dQ = \left[\int_{q_{j,x}} \int_{q_{j,y}} \int_{q_{j,z}} dq_{j,x} dq_{j,y} dq_{j,z} \right]^N = [V]^N,$$

and as a result we get

$$\langle (p_{i,x}^2) \rangle = \frac{V^N \cdot \int_P \cdots [p_{i,x}^2] \cdot \exp(-\beta\mathcal{H}) \cdot dP}{V^N \cdot \int_P \cdots \exp(-\beta\mathcal{H}) \cdot dP}. \quad (\text{B.29})$$

The remaining integrals in (B.29) are of a standard form and are worked out in detail in (A.18) → (A.22), which, in particular, say

⁵For example, such as the gravity.

$$\int_{-\infty}^{+\infty} \exp(-\alpha p^2) dp = \sqrt{\frac{\pi}{\alpha}},$$

$$\int_{-\infty}^{+\infty} p^2 \exp(-\alpha p^2) dp = \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}}. \quad (\text{B.30})$$

Therefore, in the following only a brief description is provided. First, let us look at the denominator in (B.28) and (B.29). Although we need to calculate only a part of this integral for the present purposes – see below – with a view to using it later, is worked out in toto here.

The denominator of the right hand side of (B.29) is the following:

$$\left(\frac{V}{h^3}\right)^N \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} dp_{1,x} dp_{1,y} dp_{1,z} \dots dp_{N,x} dp_{N,y} dp_{N,z}$$

$$\times \exp\left(\frac{-\beta\{p_{1,x}^2 + p_{1,y}^2 + p_{1,z}^2 + \dots + p_{N,x}^2 + p_{N,y}^2 + p_{N,z}^2\}}{2m}\right). \quad (\text{B.31})$$

The $3N$ seemingly different integrals in (B.31) that are being multiplied together are all equal. Therefore, their product can be written very simply as follows:

$$\left(\frac{V}{h^3}\right)^N \left[\int_{-\infty}^{\infty} \exp\left(\frac{-\beta p^2}{2m}\right) dp\right]^{3N} = \left(\frac{V}{h^3}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}. \quad (\text{B.32})$$

To deal with the numerator of (B.29), let us separate the integral that is taken over the variable $p_{i,x}$, i.e.,

$$\int_{-\infty}^{\infty} [p_{i,x}^2] \exp\left(\frac{-\beta\{p_{i,x}^2\}}{2m}\right) dp_{i,x},$$

from the rest of the $(3N-1)$ integrals. We get:

$$\left(\frac{V}{h^3}\right)^N \cdot \int_Q \dots \int_P [p_{i,x}^2] \cdot \exp(-\beta\mathcal{H}) \cdot dP$$

$$= \left(\frac{V}{h^3}\right)^N \cdot \left(\int_{-\infty}^{\infty} [p_{i,x}^2] \exp\left(\frac{-\beta\{p_{i,x}^2\}}{2m}\right) dp_{i,x}\right) \cdot$$

$$\left[\int_{-\infty}^{\infty} \exp\left(\frac{-\beta p^2}{2m}\right) dp\right]^{3N-1}$$

$$\begin{aligned}
&= \left(\frac{V}{h^3}\right)^N \cdot \left(\frac{1}{2} \sqrt{\frac{\pi}{\left(\frac{\beta}{2m}\right)^3}}\right) \cdot \left[\frac{\pi}{\frac{\beta}{2m}}\right]^{\frac{(3N-1)}{2}} \\
&= \left(\frac{V}{h^3}\right)^N \cdot \left(\frac{1}{2} \sqrt{\pi} \left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\right) \cdot \left[\frac{2m\pi}{\beta}\right]^{\frac{3N-1}{2}}. \tag{B.33}
\end{aligned}$$

Equation (B.33) gives the numerator of the right hand side of (B.29). As is clear from (B.29), to determine the thermodynamic average $\langle p_{i,x}^2 \rangle$, we need to divide the result obtained in (B.33) by that found in (B.31) and (B.32). Further, because the system is isotropic, we get:

$$\begin{aligned}
\langle p_{i,x}^2 \rangle &= \frac{\langle p_{i,x}^2 \rangle + \langle p_{i,y}^2 \rangle + \langle p_{i,z}^2 \rangle}{3} = \frac{\langle \mathbf{p}_i^2 \rangle}{3} \\
&= \frac{\left(\frac{V}{h^3}\right)^N \cdot \frac{1}{2} \sqrt{\pi} \left(\frac{2m}{\beta}\right)^{\frac{3}{2}} \cdot \left(\frac{2m\pi}{\beta}\right)^{\frac{3N-1}{2}}}{\left(\frac{V}{h^3}\right)^N \cdot \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}} = \frac{m}{\beta} = k_B T m. \tag{B.34}
\end{aligned}$$

We notice that $\langle \mathbf{p}_i^2 \rangle$ is independent of the position i of the i -th particle. Thus we can write

$$3 \langle p_{i,x}^2 \rangle = \langle \mathbf{p}_i^2 \rangle = \langle \mathbf{p}^2 \rangle. \tag{B.35}$$

Therefore, according to (B.27) and (B.34), the internal energy of a perfect gas consisting of N atoms is equal to:

$$U = \langle \mathcal{H} \rangle = N \frac{\langle \mathbf{p}^2 \rangle}{2m} = \frac{3N}{2} k_B T. \tag{B.36}$$

Appendix C

Second Law: Carnot Version Leads to Clausius Version

Carnot's ideas revolutionized the physics of heat engines. The formulation of the necessary ingredients for achieving maximum efficiency, inspired Lord Kelvin to attempt to understand the true meaning of "temperature." Indeed, some would say that "Absolute Temperature" and the relevant "Kelvin Scale" were owed directly to this understanding.

Another milestone in the history of thermodynamics is the Second Law. It turns out, however, that the Carnot law, the absolute temperature scale, and the second law are all closely related. And the Carnot statement in fact leads to the second law.

To analyze these issues we consider two engines in tandem: one a perfect Carnot engine and the other an engine of ordinary variety. In this fashion we prove that violation of the Carnot version of the second law leads to a physically unacceptable conclusion: namely, that without external assistance a positive amount of heat energy can be extracted from a cold dump and all of it transferred to a hot reservoir. Clearly, therefore, a violation of the Carnot version of the second law necessarily results in a violation of the Clausius version of the second law.

C.1 A Carnot and an Ordinary Engine in Tandem

Let T_H and T_C be the temperatures of the hot reservoir and the cold dump, respectively.

Consider an "ordinary" cyclic engine. As usual, each cycle comprises four legs. But, unlike a perfect Carnot engine, here at least one – but possibly all – of the four legs, are traversed either wholly or partially irreversibly.

Arrange the ordinary engine so that it withdraws heat energy $Q'(T_H)$ from the hot reservoir at temperature T_H , and $Q'(T_C)$ from the cold dump at the lower temperature T_C . As usual, set this engine up so that it works in the forward direction, and does positive amount of work, W' . The work done per cycle is equal to the total heat energy input into the working substance during the two isothermal legs. Therefore,

$$W' = Q'(T_H) + Q'(T_C). \quad (\text{C.1})$$

Also, get hold of a perfect Carnot engine but arrange it to work “backwards”! Realize that a perfect Carnot engine, much like any other engine, can be run forwards or backwards.

A backward running perfect Carnot engine withdraws negative amount of heat energy equal to $-Q^{\text{rev}}(T_H)$, from the hot reservoir during the isothermal leg at temperatures T_H . Similarly, it withdraws a negative amount of heat energy $-Q^{\text{rev}}(T_C)$, from the cold dump during the isothermal leg at temperature T_C . Arrange things so that as a result of withdrawing negative amount of heat energy during both the isothermal legs, the work W^{rev} done, per cycle, by the perfect Carnot engine, i.e.,

$$W^{\text{rev}} = -Q^{\text{rev}}(T_H) - Q^{\text{rev}}(T_C),$$

is equal to the negative of the work, W' , done per cycle by the ordinary engine described in (C.1) above.¹ That is

$$W^{\text{rev}} = -W'. \quad (\text{C.2})$$

Using (C.1), we can represent the efficiency, ϵ' , of the ordinary engine as follows:

$$\epsilon' = \frac{W'}{Q'(T_H)}. \quad (\text{C.3})$$

Similarly, (C.2) leads to the following expression for the efficiency, ϵ_{carnot} , of the perfect Carnot engine:

$$\epsilon_{\text{carnot}} = \left[\frac{W^{\text{rev}}}{-Q^{\text{rev}}(T_H)} \right] = \frac{-W^{\text{rev}}}{Q^{\text{rev}}(T_H)} = \frac{W'}{Q^{\text{rev}}(T_H)}. \quad (\text{C.4})$$

Now, if the following inequality were ever true,

$$\epsilon' > \epsilon_{\text{carnot}}, \quad (\text{C.5})$$

it would violate the Carnot version of the second law. Using (C.3) and (C.4), the disallowed inequality (C.5) can also be represented as

$$\frac{W'}{Q'(T_H)} > \frac{W'}{Q^{\text{rev}}(T_H)}. \quad (\text{C.6})$$

¹In general, it is always possible to arrange for this to happen. For instance, according to (4.9), (4.10) and (4.16), when the working substance is ideal gas, for prescribed values of T_H and T_C , V_1 and V_2 determine the values of the heat energy exchanges and therefore the amount of work done.

Multiplying both sides by $Q^{\text{rev}}(T_H) \cdot Q'(T_H)$, the inequality (C.6) becomes

$$Q^{\text{rev}}(T_H) - Q'(T_H) > 0. \quad (\text{C.7})$$

(Although different looking, in fact the inequality (C.7) is a re-statement of the inequality (C.5).) Thus, if the inequality (C.7) were ever true, the Carnot version of the second law would be violated.

We recall that the two sums

$$\left[Q'(T_H) + Q'(T_C) \right],$$

and

$$\left[Q^{\text{rev}}(T_H) + Q^{\text{rev}}(T_C) \right],$$

have been set – see (C.1) and (C.2) – to be equal, i.e.,

$$Q'(T_H) + Q'(T_C) = Q^{\text{rev}}(T_H) + Q^{\text{rev}}(T_C).$$

Let us represent this fact in the following form:

$$Q'(T_C) - Q^{\text{rev}}(T_C) = Q^{\text{rev}}(T_H) - Q'(T_H). \quad (\text{C.8})$$

Using (C.8), the inequality given in (C.7) also leads to the following inequality:

$$Q'(T_C) - Q^{\text{rev}}(T_C) > 0. \quad (\text{C.9})$$

The inequalities (C.7) and (C.9) are of fundamental interest and are needed in the discussion that follow later.

Let us now enclose the two engines inside an isolating, adiabatic chamber and run the two in tandem. Remember, the two engines consist of, one ordinary engine – described by (C.1) – that is working in the forward direction, and one perfect Carnot engine working backwards as described by (C.2).

The tandem mode of operation is described by the sum of (C.1) and (C.2). It is important to note that the two engines working in tandem in the manner described, manage to do no work at all ! That is

$$\left[Q'(T_H) + Q'(T_C) \right] - \left[Q^{\text{rev}}(T_H) + Q^{\text{rev}}(T_C) \right] = W' - W' = 0. \quad (\text{C.10})$$

Re-arranging (C.10) – or, equivalently, (C.8) – gives

$$\left[Q'(T_C) - Q^{\text{rev}}(T_C) \right] = - \left[Q'(T_H) - Q^{\text{rev}}(T_H) \right]. \quad (\text{C.11})$$

Let us pause to consider the message contained in (C.11) with some care.

The left hand side represents the heat energy isothermally “added by the dump” – which is at temperature T_C – “into the working substance of the two engines operating in tandem.”² And, if the inequality (C.9) holds – meaning, if the Carnot statement of the second law is violated – then this heat energy is positive. So where did this positive amount of heat energy go? Because no work has been done, and the fact that the tandem engine is operating within an adiabatic enclosure, all of this positive amount of heat energy, supplied by the low temperature dump, must have been “transferred to the hot reservoir maintained at the higher temperature T_H .” And this is exactly what is demonstrated by the right hand side of (C.11). (To double-check on this last statement, see the inequality (C.7).) The above findings may be summarized as follows:

Violation of the Carnot version of the second law leads to a physically unacceptable conclusion: namely, that without external assistance a positive amount of heat energy can be extracted from a cold dump and all of it transferred to a hot reservoir. Thus, a violation of the Carnot version of the second law necessarily results in a violation of the Clausius version of the second law.

²Do not forget that the tandem operation consists of a forwards working ordinary engine and a backwards operating Carnot engine.

Appendix D

Positivity of the Entropy Increase: (4.73)

According to (4.73), in order to demonstrate the positivity of the total increase of the entropy for general values of M_H and M_S one needs to show that the following is true:

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_c + \Delta S_h = \ln \left(\frac{T_f}{T_c} \right)^{M_c} + \ln \left(\frac{T_f}{T_h} \right)^{M_h} \\ &= \ln \left[\left(\frac{T_f}{T_c} \right)^{M_c} \times \left(\frac{T_f}{T_h} \right)^{M_h} \right] \geq 0. \end{aligned} \quad (\text{D.1})$$

Equivalently, the validity of the following inequality needs to be proven.

$$\left[\left(\frac{T_f}{T_c} \right)^{M_c} \times \left(\frac{T_f}{T_h} \right)^{M_h} \right] \geq 1. \quad (\text{D.2})$$

In what follows in the present appendix, we prove the validity of the inequality (D.2).

D.1 Analysis

Transferring T_c and T_h to the right hand side, we get a convenient form for this inequality.

$$T_f \geq \left[(T_c)^{\frac{M_c}{M_c + M_h}} \times (T_h)^{\frac{M_h}{M_c + M_h}} \right]. \quad (\text{D.3})$$

In order to demonstrate the validity of the above inequality it is helpful to introduce some notational changes. For convenience, we shall use the following notation:

$$\beta = \left(\frac{M_h}{M_c} \right) > 0; \alpha = \frac{T_h}{T_c} \geq 1; z = \left(\frac{M_h}{M_c + M_h} \right) = \frac{\beta}{1 + \beta}. \quad (\text{D.4})$$

[Note, that z given above lies within the range $1 > z > 0$. Also, that because both M_h and M_c are positive, so is their ratio β .]

Using the notation introduced above in (D.4), (4.70) can be written as

$$\begin{aligned} (T_f) &= \frac{(M_c T_c + M_h T_h)}{(M_c + M_h)} = M_c T_c \left(\frac{(1 + \frac{M_h T_h}{M_c T_c})}{M_c + M_h} \right) = T_c \left(\frac{1 + \beta \alpha}{1 + \beta} \right) \\ &= T_c \left[\left(\frac{1}{1 + \beta} \right) + z \alpha \right] = T_c (1 - z + z \alpha). \end{aligned} \quad (\text{D.5})$$

Similarly,

$$\left[(T_c)^{\frac{M_c}{M_c + M_h}} \times (T_h)^{\frac{M_h}{M_c + M_h}} \right]$$

can be re-cast as

$$T_c^{\frac{1}{1+\beta}} \times T_h^{\frac{\beta}{1+\beta}} = T_c \left(\frac{T_h}{T_c} \right)^{\frac{\beta}{1+\beta}} = T_c \alpha^z. \quad (\text{D.6})$$

We can now re-state the positivity requirement for ΔS_{total} , last represented in (D.3), in a very compact form as follows:

$$1 - z + z \alpha \geq \alpha^z$$

or equivalently as¹

$$f(\alpha, z) = 1 - z + z \alpha - \alpha^z \geq 0. \quad (\text{D.7})$$

We notice that when $\alpha = 1$, the equality obtains and there is no change in the total entropy. This, of course, is the trivial case where T_h is equal to T_c . Similarly trivial are the cases for $z = 0$ and $z \rightarrow 1$ which arise when either the mass or the specific heat is zero in the expressions M_h or M_c . Another fact to remember is that when $z = 0.5$ the general inequality reduces to the one already treated above in (4.76).

To begin the demonstration of the validity of the general inequality given in (D.7) let us consider first the case where $\alpha = 1 + \epsilon$ with $\epsilon \ll 1$. Then for all values of z lying within its allowed domain the inequality must hold because

$$f(1 + \epsilon, z) = z(1 - z) \frac{\epsilon^2}{2} > 0. \quad (\text{D.8})$$

Next we look at the rate of change of $f(\alpha, z)$ with respect to α . That is

$$\frac{df(\alpha, z)}{d\alpha} = z - \frac{z}{\alpha^{1-z}}. \quad (\text{D.9})$$

¹To see this, first replace the left hand side of (D.3) by the right hand side of (D.5). Next, replace the right hand side of (D.3) by the right hand side of (D.6). Finally, cancel the multiplying factor T_c from both sides.

Now, because $\alpha > 1$ and $1 - z$ is positive

$$\alpha^{1-z} > 1, \tag{D.10}$$

within the specified domains for α and z . This fact insures the positivity of the slope $\frac{df(\alpha, z)}{d\alpha}$. And beginning with $\alpha = 1 + \epsilon$, where $f(\alpha, z)$ is positive, the positivity of the slope insure the positivity of $f(\alpha, z)$ itself. That is, of course, within the specified domain for α and z : namely, $\alpha \geq 1$ and $1 > z > 0$.

Appendix E

Mixture of Van der Waals Gases

Because of the great historical importance of the Van der Waals theory of imperfect gases, and the impetus it provided to the development of thermodynamics, it is in order to ask how would the equation of state change for a mixture of different Van der Waals gases. In particular, would the mixture preserve the Dalton's law of partial pressures?

In this appendix, we show that the equation of state for a mixture of Van der Waals gases remains unchanged in form. However, despite its similarity to the equation of state of an unmixed Van der Waals fluid, Dalton's law of partial pressures is not necessarily valid for a mixture of dissimilar gases.

E.1 Analysis

If the gases being mixed have no inter-molecular interaction, the equation of state for the mixture is simply found.

$$PV = (N_1 + N_2)k_B T = (n_1 + n_2)RT, \quad (\text{E.1})$$

where N_1 , N_2 , or n_1 , n_2 represent the number of molecules, or the number of moles, in the two gases. As for a single gas, when interactions are taken into account au Van der Waals, we expect both the pressure P and the volume V to get modified.

Let us treat first the attractive part of the potential. As for a single type of molecular pair, we assume the range of interaction to be practically infinite for all molecular pairs. Thus, the mutual potential energy of any pair of molecules, separated by more than the hard core radius, is independent of their separation. Accordingly, the total mutual potential energy, E_{11} , of the N_1 molecules of the first Van der Waals gas is proportional to the number of distinct pairs of the first type of molecules. That is

$$E_{11} \propto -\frac{N_1(N_1 - 1)}{2}. \quad (\text{E.2})$$

As noted earlier, this negative potential energy results in an attractive force between molecules that leads to a reduction in the pressure which in the limit $N_1 \gg 1$ can be expressed as

$$Z_{11}(V) N_1^2/2, \quad (\text{E.3})$$

where $N_1^2/2$ is the number of distinct molecular pairs of the first type of molecules and $Z_{11}(V)$ is a function of V and positive.

Of course, the mutual potential energy of the second type of molecules would also cause a correspondingly similar reduction in pressure, namely

$$Z_{22}(V) N_2^2/2, \quad (\text{E.4})$$

where $Z_{22}(V)$ is a function of V and positive. Also, we have made the approximation $N_2 \gg 1$.

Similarly, the attractive interaction between the two different type of molecules would be proportional to the number of distinct pairs that can be formed. Note that this number is $N_1 \times N_2$. The corresponding reduction in pressure would therefore be

$$Z_{12}(V) N_1 N_2. \quad (\text{E.5})$$

Because P is an intensive state variable, in the limit $(N_1 + N_2) \gg 1$ it is independent of $N_1 + N_2$. Similarly, V is an extensive state variable, therefore in this limit it scales linearly with $N_1 + N_2$. Clearly, therefore, all three $Z(V)$'s must scale as

$$Z(V) \propto \frac{1}{V^2}, \quad (\text{E.6})$$

leading to the following expression for the change in pressure

$$\begin{aligned} \delta P &= -Z_{11}(V) N_1^2/2 - Z_{22}(V) N_2^2/2 - Z_{12}(V) N_1 N_2 \\ &= -z_{11} \frac{N_1^2}{V^2} - z_{22} \frac{N_2^2}{V^2} - 2z_{12} \frac{N_1 N_2}{V^2}, \end{aligned} \quad (\text{E.7})$$

where we introduced the notation

$$\frac{Z_{11}(V)}{2} = \frac{z_{11}}{V^2}; \quad \frac{Z_{22}(V)}{2} = \frac{z_{22}}{V^2}; \quad \frac{Z_{12}(V)}{2} = \frac{z_{12}}{V^2}. \quad (\text{E.8})$$

Similar to the case where all molecules were identical, the phenomenological constants z_{11}, z_{22}, z_{12} are all positive.

As before, it is convenient to work in molal units, and use the notation that includes the Avogadro's number N_A .

$$\begin{aligned} N_1 &= n_1 N_A; \quad N_2 = n_2 N_A \\ z_{11} N_A^2 &= a_{11}; \quad z_{22} N_A^2 = a_{22} \\ z_{12} N_A^2 &= a_{12}; \quad V = (n_1 + n_2)v. \end{aligned} \quad (\text{E.9})$$

Therefore, in complete analogy with the Van der Waals gas for only one type of molecules with interaction parameter a , for the mixed gas we can also define an – effective – interaction parameter a' ,

$$\Delta P = -\frac{a'}{v^2}, \quad (\text{E.10})$$

where

$$a' = \left(\frac{a_{11} n_1^2 + a_{22} n_2^2 + 2 a_{12} n_1 n_2}{(n_1 + n_2)^2} \right). \quad (\text{E.11})$$

The hard core part of the potential can also be treated in an analogous manner. As before, the two types of molecules are assumed incompressible, spherical hard-balls of radii r_1 and r_2 .

Consider a pair of type 1 molecules. The nearest distance that their centers can get to is $2r_1$. Accordingly, for each molecule, the equivalent of half of the spherical volume – that is $= \frac{1}{2} \cdot \frac{4\pi}{3} (2r_1)^3$ – is excluded. Therefore, the contribution to the total excluded volume due to short range repulsion *only between type 1 molecules* is given by

$$N_1 \left[\frac{1}{2} \times \frac{4\pi}{3} (2r_1)^3 \right] \times \left(\frac{N_1}{N_1 + N_2} \right). \quad (\text{E.12})$$

Note that when there are only a single type of molecules present, i.e., $N_2 = 0$, we retrieve the earlier result. When the second type of molecules are also there, we do need the weighting factor described by the second term, namely $\left(\frac{N_1}{N_1 + N_2} \right)$, which determines the probability for a chosen molecule to actually be of type 1.

Following the same argument, the contribution to the total excluded volume due to the short range repulsion only between type 2 molecules is given by

$$N_2 \left[\frac{1}{2} \times \frac{4\pi}{3} (2r_2)^3 \right] \times \left(\frac{N_2}{N_1 + N_2} \right). \quad (\text{E.13})$$

The excluded volume due to the avoidance of hard cores overlap for a type 1-type 2 pair is found as follows. The diameter of the excluded sphere is now $r_1 + r_2$. Also, as mentioned above, rather than being $N_1^2/2$ or $N_2^2/2$, for this case the number of distinct pairs is a function of both N_1 and N_2 . Thus, we may represent this part of the excluded volume as

$$\alpha(N_1, N_2) \times \left[\frac{1}{2} \times \frac{4\pi}{3} (r_1 + r_2)^3 \right]. \quad (\text{E.14})$$

The constant $\alpha(N_1, N_2)$ can be determined either by careful argument or a dimensional approach. Below we pursue the latter course because it is both shorter and easier to understand.

Adding the three contributions to the excluded volume we get

$$\begin{aligned}
 & N_1 \left[\frac{1}{2} \times \frac{4\pi}{3} (2r_1)^3 \right] \times \left(\frac{N_1}{N_1 + N_2} \right) \\
 & + N_2 \left[\frac{1}{2} \times \frac{4\pi}{3} (2r_2)^3 \right] \times \left(\frac{N_2}{N_1 + N_2} \right) \\
 & + \alpha(N_1, N_2) \times \left[\frac{1}{2} \times \frac{4\pi}{3} (r_1 + r_2)^3 \right]. \tag{E.15}
 \end{aligned}$$

Clearly, when $r_1 = r_2 = r_o$, the distinction between the two types of molecules disappears. Accordingly, this entire expression should reduce to that obtained earlier for molecules of a single type which number $N = N_1 + N_2$. This requirement is satisfied if

$$\left(\frac{N_1^2 + N_2^2}{N_1 + N_2} \right) + \alpha(N_1, N_2) = N_1 + N_2. \tag{E.16}$$

Thus, we are immediately led to the result

$$\alpha(N_1, N_2) = \left(\frac{2 N_1 N_2}{N_1 + N_2} \right). \tag{E.17}$$

Therefore, to correct for hard core repulsion, the volume V in the ideal gas equation of state has to be changed to $(V - \Delta V)$ where

$$\begin{aligned}
 \Delta V &= (n_1 + n_2) b'; \\
 b' &= \left(\frac{b_{11} n_1^2 + b_{22} n_2^2 + 2 b_{12} n_1 n_2}{(n_1 + n_2)^2} \right) \tag{E.18}
 \end{aligned}$$

and

$$b_{11} = N_A \frac{2\pi}{3} (2r_1)^3; \quad b_{22} = N_A \frac{2\pi}{3} (2r_2)^3; \quad b_{12} = N_A \frac{2\pi}{3} (r_1 + r_2)^3. \tag{E.19}$$

[See Figs. E.1 a–d above.]

To sum up: The equation of state for a mixture of Van der Waals fluids remains unchanged in form. That is, it can still be represented as:

$$\left(P + \frac{a'}{v^2} \right) (v - b') = RT, \tag{E.20}$$

where a' and b' are the effective interaction and hard core exclusion parameters of the mixture. It is easy to check that despite this similarity, unless $a_{11} = a_{12} = a_{22}$ and $b_{11} = b_{12} = b_{22}$ Dalton's law of partial pressures is not necessarily valid. for the mixture.

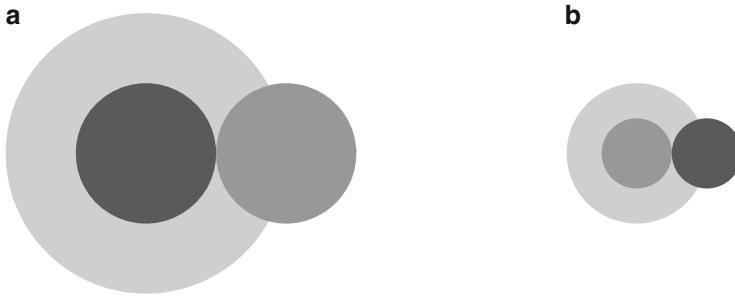


Fig. E.1 Hard Core Sphere of Exclusion for Homogeneous Pairs. **(a)** In a mixed gas composed of molecules with radii r_1 and r_2 , the size of the sphere of exclusion depends on the nature of the neighboring pairs. For pairs of type (1) molecules the sphere of exclusion has radius $2r_1$. Similarly, for pairs of type (2) molecules, the radius of the sphere of exclusion is $2r_2$. **(b)** The shading for the molecules is either dark or grey. The excluded volume is shaded very light-grey. **(c)** In a mixed gas composed of molecules with radii r_1 and r_2 , the size of the sphere of exclusion depends on the nature of the neighboring pair. When the pair consists of different types of molecules, the excluded volume is a sphere of radius $r_1 + r_2$. **(d)** Such a sphere – shaded very light-grey – can equivalently be considered to reside on either of the two molecules

Appendix F

Positive-Definite Homogeneous Quadratic Form

A change of variable can always be devised to reduce an homogeneous, symmetric quadratic form Q_n of the type

$$Q_n = \tilde{\mathbf{x}} \hat{\mathbf{a}} \mathbf{x} = \sum_{i,j}^n x_i a_{i,j} x_j. \quad (\text{F.1})$$

to a sum of squares.¹ In (F.1), x_i 's are assumed to be real and $a_{ij} = a_{ji}$.

F.1 Analysis

To see how this may be done, let us introduce a variable ξ_1

$$\xi_1 = x_1 + \frac{a_{12}}{a_{11}} x_2 + \cdots + \frac{a_{1n}}{a_{11}} x_n. \quad (\text{F.2})$$

Now, subtract $a_{11}\xi_1^2$ from Q_n . This eliminates all terms that involve x_1 . In a similar fashion, a second variable ξ_2 can then be introduced to eliminate all terms containing x_2 . Following this process, eventually one obtains

¹Note that by using a linear transformation the vector $\tilde{\mathbf{x}}$ can be transformed to another set of variables. Thus, the reduction to sum of squares can be done in innumerable ways. This does not affect the substance of the requirement for positive-definiteness as long as the transformation is non-singular. Indeed, irrespective of the choice of variables, the number of positive, zero, or negative coefficients does not change. Note, the objective of the current exercise is to affect a transformation that reduces the quadratic form to a sum of squares. For positivity of the form, every one of the coefficients multiplying the square terms must therefore be positive. See, for instance, Harold and B. S. Jeffreys, *Methods of Mathematical Physics*, page 137, Cambridge University Press (1957) and references cited there.

$$Q_n = a_{11}\xi_1^2 + b_2\xi_2^2 + \dots + b_{n-1}\xi_{n-1}^2 + b_n x_n^2, \tag{F.3}$$

where ξ_j contains terms that involve x_i 's for $i \geq j$.

F.2 Positive Definiteness of 3 x 3 Quadratic Form

It is helpful to demonstrate in detail the procedure described above. To this end, we append below the case for $n = 3$.

Let² us look at Q_3 .

$$Q_3 = \sum_{i,j}^3 x_i a_{i,j} x_j$$

$$= [a_{11} x_1^2 + 2a_{12} x_1 x_2 + 2 a_{13} x_1 x_3] + 2a_{23}x_2x_3 + a_{22}x_2^2 + a_{33}x_3^2.$$

To eliminate x_1 from the above equation, define

$$\xi_1 = x_1 + \left(\frac{2 a_{12}}{2a_{11}}\right) x_2 + \left(\frac{2 a_{13}}{2a_{11}}\right) x_3. \tag{F.4}$$

Next, calculate $a_{11}\xi_1^2$ and subtract it from Q_3 . This leads to the following, where x_1 has been eliminated.

$$Q_3 - a_{11}\xi_1^2 = \left[\frac{(a_{11}a_{22} - a_{12}^2)}{a_{11}} x_2^2 + \frac{(a_{11}a_{23} - a_{12}a_{13})}{a_{11}} 2 x_2 x_3 \right]$$

$$+ \frac{(a_{11} a_{33} - a_{13}^2)}{a_{11}} x_3^2. \tag{F.5}$$

Next, we need to eliminate x_2 . To this end, much like what we did earlier, we choose:

$$\xi_2 = x_2 + \frac{2 \left(\frac{a_{11} a_{23} - a_{12} a_{13}}{a_{11}} \right)}{2 \left(\frac{a_{11} a_{22} - a_{12}^2}{a_{11}} \right)} x_3. \tag{F.6}$$

Then, much as was done before, we calculate $\frac{(a_{11} a_{22} - a_{12}^2)}{a_{11}} \xi_2^2$ and write

²Note, square brackets will be inserted here to assist the reader in recognizing the pattern used for introducing the variables ξ_i .

$$Q_3 = a_{11}\xi_1^2 + \frac{(a_{11}a_{22} - a_{12}^2)}{a_{11}}\xi_2^2 + \frac{(a_{11}a_{22}a_{33} - a_{12}^2a_{33} - a_{13}^2a_{22} - a_{11}a_{23}^2 + 2a_{12}a_{13}a_{23})}{(a_{11}a_{22} - a_{12}^2)}x_3^2.$$

Note that in addition to x_1 we have now also excluded x_2 . There is no need to bother about excluding x_3 because it occurs only as a square which is exactly the form we are looking for. Note that the last variable – which is x_3 here – will always occur in the squared format.

For Q_3 to be positive definite, the coefficients of the square terms have to be positive definite. That is

$$a_{11} > 0, \quad (\text{F.7})$$

$$\frac{(a_{11}a_{22} - a_{12}^2)}{a_{11}} > 0, \quad (\text{F.8})$$

and

$$\frac{(a_{11}a_{22}a_{33} - a_{12}^2a_{33} - a_{13}^2a_{22} - a_{11}a_{23}^2 + 2a_{12}a_{13}a_{23})}{(a_{11}a_{22} - a_{12}^2)} > 0. \quad (\text{F.9})$$

Note, the denominators of (F.8) and (F.9) are positive because of the preceding inequalities given in (F.7) and (F.8), respectively.

All the three inequalities (F.7), (F.8) and (F.9) can more conveniently be displayed as determinants.

$$|\mathbf{A}_1| = a_{11} > 0, \quad (\text{F.10})$$

$$|\mathbf{A}_2| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} > 0, \quad (\text{F.11})$$

and

$$|\mathbf{A}_3| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} > 0. \quad (\text{F.12})$$

Note that $|\mathbf{A}_1|$, $|\mathbf{A}_2|$, and $|\mathbf{A}_3|$ are principal minors of $\hat{\mathbf{a}}$. Indeed, it turns out³ that positive definiteness of such a quadratic form for general n is assured if all the principal minors of the determinant – of the $n \times n$ matrix of the quadratic form – are positive-definite.

F.2.1 A Helpful Surprise

In the following appendix – i.e., appendix G – we study a thermodynamic system that generates a 3×3 homogeneous, symmetric quadratic form. For this system,

³See footnote 1.

the substance of the inequalities (F.10) and (F.11) – that involve differentiation with respect to only the two variables x_1 and x_2 – is readily unraveled and we are led to two eminently simple physical dictates for thermodynamic stability: namely that the specific heat C_V and the isothermal compressibility χ_T must both be positive definite. On the other hand, the analysis of the rather fierce looking inequality (F.12) – which involves nine terms – is much more involved. It is, however, noted that:

1. The given quadratic form can just as easily be represented as

$$Q_3 = \{x_3, x_2, x_1\} \cdot \hat{\mathbf{b}} \cdot \begin{Bmatrix} x_3 \\ x_2 \\ x_1 \end{Bmatrix} > 0, \quad (\text{F.13})$$

where

$$\hat{\mathbf{b}} = \begin{pmatrix} a_{33} & a_{32} & a_{31} \\ a_{23} & a_{22} & a_{21} \\ a_{13} & a_{12} & a_{11} \end{pmatrix}. \quad (\text{F.14})$$

According to this representation, positive definiteness of Q_3 is assured if

$$|\mathbf{B}_1| = a_{33} > 0, \quad (\text{F.15})$$

$$|\mathbf{B}_2| = \begin{vmatrix} a_{33} & a_{32} \\ a_{23} & a_{22} \end{vmatrix} > 0, \quad (\text{F.16})$$

and

$$|\mathbf{B}_3| = \begin{vmatrix} a_{33} & a_{32} & a_{31} \\ a_{23} & a_{22} & a_{21} \\ a_{13} & a_{12} & a_{11} \end{vmatrix} = |\mathbf{A}_3| > 0. \quad (\text{F.17})$$

2. Note that the corresponding terms equivalent to the current inequality (F.15) appear to irreducibly involve only the third linearly independent variable x_3 . Thus, a complete description of the positive definiteness of Q_3 is provided by the already disentangled two inequalities (F.10) and (F.11), and the simple third inequality given in (F.15). (See (G.18) for details.)

Appendix G

Thermodynamic Stability: Three Extensive Variables

In an earlier analysis – see (9.38) – the requirement that under appropriate conditions the system energy is a minimum was used to predict the stability criteria of a simple system. We found that for intrinsic thermodynamic stability, both the specific heat at constant volume and the isothermal compressibility must be positive. That is the following must hold:

$$C_v > 0; \chi_t > 0. \tag{G.1}$$

The first requirement, namely, $C_v > 0$, has an obvious physical basis: When heat energy is not allowed to be used for expanding the volume, all that any addition of heat energy can do is increase the system temperature.

The positivity of the isothermal compressibility χ_t is testified to by observation. When the temperature is held constant, increase in compression shrinks the volume of the object being compressed.

In this appendix, we consider an isolated system composed of a single chemical constituent with variable mole number. The variability of the mole number introduces n as an additional extensive variable. Accordingly, as shown below, the conditions for intrinsic stability also include a third requirement: namely,

$$\left(\frac{\partial \mu}{\partial n} \right)_{S,v} > 0. \tag{G.2}$$

Much like the first two requirements, the third requirement also has an obvious physical basis. In order to maintain thermodynamic equilibrium, addition of molecules, to an otherwise isolated system in equilibrium, must increase their chemical potential. A hint of this phenomenon was already noted in the chapter on “Zeroth Law; Motive Forces; Stability” – See (9.12) – where we observed that the chemical potential is higher in a region of higher particle density.

G.1 Energy Minimum Procedure: Intrinsic Stability

To satisfy the energy minimum extremum, the following two requirements must be satisfied:

$$(dU)_{S,V,n} = 0, \quad (\text{G.3})$$

$$(d^2U)_{S,V,n} > 0. \quad (\text{G.4})$$

Note, now the internal energy U is considered to be a function of three independent variables S , V and n . That is:

$$U = U(S, V, n). \quad (\text{G.5})$$

According to the first-second law:

$$\begin{aligned} dU(S, V, n) &= \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{V,S} dn \\ &= TdS - PdV + \mu dn. \end{aligned} \quad (\text{G.6})$$

The first requirement, given in (G.3), has already been fully explored and exploited in the chapter titled “Equilibrium, Motive Forces, and Stability.” In order to analyze the second requirement for the energy to be a minimum – see (G.4) – it is convenient to utilize a matrix procedure and introduce compact notation. To this end, define the matrix

$$\hat{\mathbf{J}} = \begin{pmatrix} U_{SS} & U_{SV} & U_{Sn} \\ U_{VS} & U_{VV} & U_{Vn} \\ U_{nS} & U_{nV} & U_{nn} \end{pmatrix}, \quad (\text{G.7})$$

where

$$\begin{aligned} U_{SS} &= \left(\frac{\partial^2 U}{\partial^2 S}\right)_{V,n}; U_{SV} = \left(\frac{\partial^2 U}{\partial S \partial V}\right)_n; U_{Sn} = \left(\frac{\partial^2 U}{\partial S \partial n}\right)_V; \\ U_{VS} &= \left(\frac{\partial^2 U}{\partial V \partial S}\right)_n; U_{VV} = \left(\frac{\partial^2 U}{\partial^2 V}\right)_{S,n}; U_{Vn} = \left(\frac{\partial^2 U}{\partial V \partial n}\right)_S; \\ U_{nS} &= \left(\frac{\partial^2 U}{\partial n \partial S}\right)_V; U_{nV} = \left(\frac{\partial^2 U}{\partial n \partial V}\right)_S; U_{nn} = \left(\frac{\partial^2 U}{\partial^2 n}\right)_{V,S}. \end{aligned} \quad (\text{G.8})$$

Then write

$$d^2U(S, V, n) = \{dS, dV, dn\} \cdot \hat{\mathbf{J}} \cdot \begin{Bmatrix} dS \\ dV \\ dn \end{Bmatrix} > \mathbf{0}. \quad (\text{G.9})$$

For this inequality to hold, the principal minors of the determinant $|\hat{\mathbf{J}}|$ have to be positive definite. Accordingly,

$$|\mathbf{J}_1| = U_{SS} > 0, \quad (\text{G.10})$$

$$|\mathbf{J}_2| = \begin{vmatrix} U_{SS} & U_{SV} \\ U_{VS} & U_{VV} \end{vmatrix} > 0, \quad (\text{G.11})$$

and

$$|\mathbf{J}_3| = |\hat{\mathbf{J}}| = \begin{vmatrix} U_{SS} & U_{SV} & U_{Sn} \\ U_{VS} & U_{VV} & U_{Vn} \\ U_{nS} & U_{nV} & U_{nn} \end{vmatrix} > 0. \quad (\text{G.12})$$

Now,

$$\begin{aligned} |\mathbf{J}_1| &= \left(\frac{\partial \left(\left(\frac{\partial U}{\partial S} \right)_{V,n} \right)}{\partial S} \right)_{V,n} = \left(\frac{\partial T}{\partial S} \right)_{V,n} \\ &= \left(\frac{\partial T}{\partial U} \right)_{V,n} \cdot \left(\frac{\partial U}{\partial S} \right)_{V,n} = \left(\frac{1}{C_V} \right) \cdot T > 0. \end{aligned} \quad (\text{G.13})$$

Again, much like the entropy maximum principle, the energy minimum principle requires the positivity of the specific heat C_V .

Next, let us for convenience use the Jacobian form for the inequality (G.11).

$$|\mathbf{J}_2| = \left[\frac{\partial \left(\left(\frac{\partial U}{\partial S} \right)_V, \left(\frac{\partial U}{\partial V} \right)_S \right)}{\partial (S, V)} \right]_n > 0. \quad (\text{G.14})$$

Because

$$\left(\frac{\partial U}{\partial S} \right)_{V,n} = T,$$

and

$$\left(\frac{\partial U}{\partial V} \right)_{S,n} = -P,$$

we can write

$$\begin{aligned} |\mathbf{J}_2| &= \left[\frac{\partial(T, -P)}{\partial(S, V)} \right]_n = \left[\frac{\partial(P, -T)}{\partial(V, S)} \right]_n \\ &= \left[\frac{\partial(P, -T)}{\partial(V, T)} \cdot \frac{\partial(V, T)}{\partial(V, S)} \right]_n = \left[\frac{\partial(-P, T)}{\partial(V, T)} \cdot \frac{\partial(T, V)}{\partial(S, V)} \right]_n \\ &= - \left[\left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial T}{\partial S} \right)_V \right]_n = \left[\left(\frac{1}{V\chi_T} \right) \cdot \left(\frac{T}{C_V} \right) \right]_n > 0. \end{aligned} \quad (\text{G.15})$$

Noting the already established requirement that C_V be > 0 , this inequality is satisfied only if χ_T is also > 0 .

Thus, the physical requirements for intrinsic stability in a simple isolated system are the same irrespective of whether we use the principle of entropy maximum or energy minimum.

G.1.1 Third Requirement for Intrinsic Stability

The foregoing analysis of the positivity of $|\mathbf{J}_1|$ and $|\mathbf{J}_2|$ has not been hard work. It appears, however, that the same may not be true for analyzing the positivity of the determinant $|\mathbf{J}_3|$ which has nine terms, each of which is a multiple of three different double derivatives. Therefore, in order to sail this route, we take a different tack.

As noted in Appendix G, a quadratic form of the type found in $d^2U(S, V, n)$ that is given in (G.9) can just as well be represented as follows:

$$d^2U(S, V, n) = \{dn, dV, dS\} \cdot \hat{\mathbf{K}} \cdot \begin{Bmatrix} dn \\ dV \\ dS \end{Bmatrix} > \mathbf{0}, \quad (\text{G.16})$$

where

$$\hat{\mathbf{K}} = \begin{pmatrix} U_{nn} & U_{nV} & U_{nS} \\ U_{Vn} & U_{VV} & U_{VS} \\ U_{Sn} & U_{SV} & U_{SS} \end{pmatrix} > \mathbf{0}. \quad (\text{G.17})$$

As a result, its positivity requires that the principal minors $|\mathbf{K}_1|$, $|\mathbf{K}_2|$, and $|\mathbf{K}_3|$ be positive definite. Here

$$\begin{aligned} |\mathbf{K}_1| &= U_{nn} = \left(\frac{\partial^2 U}{\partial^2 n} \right)_{S,V} = \left(\frac{\partial \left(\frac{\partial U}{\partial n} \right)_{S,V}}{\partial n} \right)_{S,V} \\ &= \left(\frac{\partial \mu}{\partial n} \right)_{S,V} > 0. \end{aligned} \quad (\text{G.18})$$

Because for given S and V , the above requirement involves only the rate of change of the chemical potential with respect to the occupancy n (of the relevant molecule), and the earlier two requirements explicitly depended only on the rates of change of the other two extensive parameters, S and V , therefore this must be the third linearly independent requirement for intrinsic stability.

A clear display of the important results is given below.

For intrinsic thermodynamic stability the following three physical requirements must be satisfied:

$$\begin{aligned}
C_V &> 0, \\
&\text{and} \\
\chi_T &> 0, \\
&\text{and} \\
\left(\frac{\partial\mu}{\partial n}\right)_{S,V} &> 0.
\end{aligned}
\tag{G.19}$$

Much like the first two requirements noted above, the third requirement also has an obvious physical basis: to maintain thermodynamic equilibrium, addition of molecules, to an otherwise isolated system in equilibrium, must increase their chemical potential. A hint of this phenomenon has already been noted in the chapter on “Zeroth Law; Motive Forces; Stability” – See (9.12) – where we observed the equivalent of the fact that the chemical potential is higher in a region of higher particle density.¹

G.2 Examples

G.2.1 Example I

Represent a row-vector of intensive variables, $\{dT, -dP, d\mu\}$, in terms of its conjugate column-vector. In other words, find the matrix $\hat{\mathbf{M}}$ that is defined by the following relationship:

$$\{dT, -dP, d\mu\} = \hat{\mathbf{M}} \cdot \begin{Bmatrix} dS \\ dV \\ dn \end{Bmatrix}.
\tag{G.20}$$

G.2.1.1 Solution

Begin with the first intensive variable on the left hand side and represent it as a function of all the extensive variables. That is,

$$T = T(S, V, n).
\tag{G.21}$$

¹For instance, compare with that statement: Simply put, the requirement that in an isolated system the entropy must increase in an isothermal spontaneous process, mandates the molecular flow, at constant temperature, to occur away from a region of higher chemical potential towards a region of lower chemical potential.

Exploit the fact that dT is an exact differential.

$$dT(S, V, n) = \left(\frac{\partial T}{\partial S}\right)_{V,n} dS + \left(\frac{\partial T}{\partial V}\right)_{S,n} dV + \left(\frac{\partial T}{\partial n}\right)_{S,V} dn. \quad (\text{G.22})$$

Now invoke the first-second law

$$TdS = dU + PdV - \mu dn, \quad (\text{G.23})$$

and note that for constant V and n

$$T(dS)_{V,n} = (dU)_{V,n}. \quad (\text{G.24})$$

Therefore,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n}. \quad (\text{G.25})$$

Introduce this expression for T in the three terms on the right hand side of (G.22) to get

$$\begin{aligned} dT(S, V, n) &= \left(\frac{\partial \left(\frac{\partial U}{\partial S}\right)_{V,n}}{\partial S}\right)_{V,n} dS + \left(\frac{\partial \left(\frac{\partial U}{\partial S}\right)_{V,n}}{\partial V}\right)_{S,n} dV + \left(\frac{\partial \left(\frac{\partial U}{\partial S}\right)_{V,n}}{\partial n}\right)_{S,V} dn \\ &= U_{SS}dS + U_{SV}dV + U_{Sn}dn. \end{aligned} \quad (\text{G.26})$$

We follow the same procedure for the remaining two intensive variables – P and μ – on the left of hand side of (G.20). Without comment, salient steps of this exercise are recorded below.

$$\begin{aligned} P &= P(S, V, n); \\ dP &= \left(\frac{\partial P}{\partial S}\right)_{V,n} dS + \left(\frac{\partial P}{\partial V}\right)_{S,n} dV + \left(\frac{\partial P}{\partial n}\right)_{S,V} dn; \\ P &= -\left(\frac{\partial U}{\partial V}\right)_{S,n}; \\ -dP &= U_{S,V}dS + U_{V,V}dV + U_{n,V}dn. \end{aligned} \quad (\text{G.27})$$

$$\begin{aligned} \mu &= \mu(S, V, n); \\ d\mu &= \left(\frac{\partial \mu}{\partial S}\right)_{V,n} dS + \left(\frac{\partial \mu}{\partial V}\right)_{S,n} dV + \left(\frac{\partial \mu}{\partial n}\right)_{S,V} dn; \\ \mu &= \left(\frac{\partial U}{\partial n}\right)_{S,V}; \\ d\mu &= U_{n,S}dS + U_{n,V}dV + U_{nn}dn. \end{aligned} \quad (\text{G.28})$$

Equations (G.26)–(G.28) are readily seen to be represented by (G.20) where

$$\hat{\mathbf{M}} = \begin{pmatrix} U_{SS} & U_{SV} & U_{Sn} \\ U_{SV} & U_{VV} & U_{nV} \\ U_{nS} & U_{nV} & U_{nn} \end{pmatrix}. \quad (\text{G.29})$$

G.2.2 Example II

Find matrix $\hat{\mathbf{H}}$ where

$$\{dT, -dV, d\mu\} = \hat{\mathbf{H}} \cdot \begin{Bmatrix} dS \\ -dP \\ dn \end{Bmatrix}. \quad (\text{G.30})$$

G.2.2.1 Solution

$$\begin{aligned} T &= T(S, P, n); \\ dT &= \left(\frac{\partial T}{\partial S}\right)_{P,n} dS + \left(\frac{\partial T}{\partial P}\right)_{S,n} dP + \left(\frac{\partial T}{\partial n}\right)_{S,P} dn; \\ T dS &= dH - V dP - \mu dn; \\ T &= \left(\frac{\partial H}{\partial S}\right)_{P,n}; \\ dT &= H_{SS} dS + U_{PS} dP + H_{nS} dn. \end{aligned} \quad (\text{G.31})$$

$$\begin{aligned} V &= V(S, P, n); \\ dV &= \left(\frac{\partial V}{\partial S}\right)_{P,n} dS + \left(\frac{\partial V}{\partial P}\right)_{S,n} dP + \left(\frac{\partial V}{\partial n}\right)_{S,P} dn; \\ V &= \left(\frac{\partial H}{\partial P}\right)_{S,n}; \\ dV &= H_{SP} dS + H_{PP} dP + H_{nP} dn. \end{aligned} \quad (\text{G.32})$$

$$\begin{aligned}
 \mu &= \mu(S, P, n); \\
 d\mu &= \left(\frac{\partial\mu}{\partial S}\right)_{P,n} dS + \left(\frac{\partial\mu}{\partial P}\right)_{S,n} dP + \left(\frac{\partial\mu}{\partial n}\right)_{S,P} dn; \\
 \mu &= \left(\frac{\partial H}{\partial n}\right)_{S,V}; \\
 d\mu &= H_{Sn}dS + H_{Pn}dP + H_{nn}dn.
 \end{aligned}
 \tag{G.33}$$

Thus

$$\hat{\mathbf{H}} = \begin{pmatrix} H_{SS} & H_{PS} & H_{nS} \\ H_{SP} & H_{PP} & H_{nP} \\ H_{Sn} & H_{Pn} & H_{nn} \end{pmatrix}.
 \tag{G.34}$$

Appendix H

Massieu Transforms: The Entropy Representation

To determine the Massieu transforms,¹ one needs to use the entropy representation.² In this representation, the entropy s acts as the central thermodynamic potential.³

H.1 Massieu Potential: $M\{v, u\}$

Let us consider, in the entropy representation, the fundamental equation for a simple thermodynamic system that is recorded in (8.18). For convenience, it is re-produced in an equivalent form below:

$$s = \left(\frac{p}{t}\right)v + \left(\frac{1}{t}\right)u - \left(\frac{\mu}{t}\right)n + \left(\frac{\mathcal{Y}}{t}\right)\mathcal{X}. \quad (\text{H.1})$$

This equation describes how the extensive variable, the entropy s , depends on other extensive variables: the volume v , the internal energy u , the mole numbers n , and extensive parameters such as \mathcal{X} . The simple system being treated here has constant number of atoms and does not have any dependence on the term $(\mathcal{Y} \mathcal{X})$. For such a system, a convenient appropriate relationship is provided by the statement of the first-second law. That statement was originally given in (5.6). Again, for convenience, we reproduce it below. (Also, compare (10.13))

$$ds = \left(\frac{p}{t}\right)dv + \left(\frac{1}{t}\right)du. \quad (\text{H.2})$$

¹Massieu, M. F.

²Corresponding work in the energy representation – called the Legendre transformations – is discussed in the chapter on Thermodynamic Potentials.

³For example, recall that, in the chapter titled “Equilibrium, Motive Forces, and Stability,” the entropy was shown to play a central role in determining thermodynamic equilibrium and stability.

Clearly, for the entropy s , the “canonical” – i.e., the characteristic – independent variables are the volume v and the internal energy u : that is,

$$s = s(v, u). \quad (\text{H.3})$$

The entropy $s(v, u)$, therefore, is itself the Massieu potential $M\{v, u\}$. That is: $s(v, u) = M\{v, u\}$.

H.1.1 Massieu Potential: $M\left\{v, \frac{1}{t}\right\}$

Rather than the internal energy u – as is the case in (H.2) above – the inverse temperature, $\left(\frac{1}{t}\right)$, is greatly preferred as an independent variable. Therefore, in (H.2), the variable of interest – that we should transform out of – is the internal energy u which occurs in the form $+\left(\frac{1}{t}\right) du$. In order to eliminate du , we transcribe $+\left(\frac{1}{t}\right) du$ as follows.

Add $-\left(\frac{1}{t}\right) u$ to the primary potential s . This introduces an alternate Massieu potential $M\left\{v, \frac{1}{t}\right\}$.

$$M\left\{v, \frac{1}{t}\right\} = s - \left(\frac{1}{t}\right) u = -\frac{f}{t}. \quad (\text{H.4})$$

(Note: $-t \cdot M\left\{v, \frac{1}{t}\right\}$ is equal to the Helmholtz free energy f . Thus $M\left\{v, \frac{1}{t}\right\}$ is really a close relative of an old, but important, thermodynamic potential.) Differentiate $M\left\{v, \frac{1}{t}\right\}$.

$$dM\left\{v, \frac{1}{t}\right\} = (ds) - \left(\frac{1}{t}\right) du - u d\left(\frac{1}{t}\right). \quad (\text{H.5})$$

And, cancel $-\left(\frac{1}{t}\right) du$ by inserting the original relationship for ds given in (H.2). That is

$$\begin{aligned} dM\left\{v, \frac{1}{t}\right\} &= \left(\frac{p}{t}\right) dv + \left(\frac{1}{t}\right) du - \left(\frac{1}{t}\right) du - u d\left(\frac{1}{t}\right) \\ &= \left(\frac{p}{t}\right) dv - u d\left(\frac{1}{t}\right). \end{aligned} \quad (\text{H.6})$$

The inverse temperature $\left(\frac{1}{t}\right)$ is the new independent variable that is conjugate to the previous independent variable the internal energy u . Note, both the characteristic independent variables here, v and $\frac{1}{t}$, are easy to measure.

H.1.2 Remark

The simple thermodynamic system being considered here provides only four possible choices for the pairs of independent characteristic variables. These are: (v, u) , $(v, \frac{1}{t})$, $(\frac{p}{t}, \frac{1}{t})$ and $(\frac{p}{t}, u)$. So far in this appendix, only two of these four pairs have been utilized: namely, (v, u) in $M\{v, u\}$; $(v, \frac{1}{t})$ in $M\{v, \frac{1}{t}\}$. To make use of the last two pairs, namely $(\frac{p}{t}, \frac{1}{t})$ and $(\frac{p}{t}, u)$, we need to proceed, in the usual fashion, as follows:

H.1.3 Massieu Potential: $M\{\frac{p}{t}, u\}$

The appropriate new thermodynamic potential is:

$$M\left\{\frac{p}{t}, u\right\} = s - \left(\frac{p}{t}\right) v. \tag{H.7}$$

Take its derivative,

$$d\left(M\left\{\frac{p}{t}, u\right\}\right) = ds - \left(\frac{p}{t}\right) dv - v d\left(\frac{p}{t}\right). \tag{H.8}$$

Now, following (H.2), replace ds by $\left(\frac{p}{t}\right) dv + \left(\frac{1}{t}\right) du$. This yields the following relationship.

$$\begin{aligned} d\left(M\left\{\frac{p}{t}, u\right\}\right) &= ds - \left(\frac{p}{t}\right) dv - v d\left(\frac{p}{t}\right) \\ &= \left(\frac{p}{t}\right) dv + \left(\frac{1}{t}\right) du - \left(\frac{p}{t}\right) dv - v d\left(\frac{p}{t}\right) \\ &= \left(\frac{1}{t}\right) du - v d\left(\frac{p}{t}\right). \end{aligned} \tag{H.9}$$

Note: The Massieu potential, $M\{\frac{p}{t}, u\}$, whose independent characteristic variables are $\frac{p}{t}$ and u , is not a “close relative” of previous thermodynamic potentials. Rather, it is a new thermodynamic potential.

H.1.4 Massieu Potential: $M\{\frac{p}{t}, \frac{1}{t}\}$

Choose the following Massieu potential:

$$\begin{aligned}
 M\left\{\frac{p}{t}, \frac{1}{t}\right\} &= M\left\{v, \frac{1}{t}\right\} - \left(\frac{p}{t}\right) v \\
 &= s - \left(\frac{1}{t}\right) u - \left(\frac{p}{t}\right) v = -\frac{g}{t}.
 \end{aligned}
 \tag{H.10}$$

(Note: $-t \cdot M\left\{\frac{p}{t}, \frac{1}{t}\right\}$ is equal to the Gibbs free energy g . Thus $M\left\{\frac{p}{t}, \frac{1}{t}\right\}$ is not a new function. Rather, it is a close relative of an old, but important, thermodynamic potential: the Gibbs free energy.) Then differentiate both sides.

$$d\left(M\left\{\frac{p}{t}, \frac{1}{t}\right\}\right) = d\left(M\left\{v, \frac{1}{t}\right\}\right) - \left(\frac{p}{t}\right) \cdot dv - v \cdot d\left(\frac{p}{t}\right).
 \tag{H.11}$$

Now, using (H.6), replace $dM\left\{v, \frac{1}{t}\right\}$ by $\left(\frac{p}{t}\right) dv - ud\left(\frac{1}{t}\right)$. This yields the desired relationship.

$$d\left(M\left\{\frac{p}{t}, \frac{1}{t}\right\}\right) = -v \cdot d\left(\frac{p}{t}\right) - u \cdot d\left(\frac{1}{t}\right).
 \tag{H.12}$$

As mentioned above, the Massieu potential $M\left\{\frac{p}{t}, \frac{1}{t}\right\}$ is not new. Rather, it is closely related to the Gibbs free energy g .

Appendix I

Integral (11.83)

We need to calculate the following:

$$\begin{aligned}
 u_i &= u \\
 &= \frac{\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2) \exp[-\beta F(1, 2)]}{\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \exp[-\beta F(1, 2)]}, \quad (I.1)
 \end{aligned}$$

where

$$F(1, 2) = - \left(\frac{C\mu_1\mu_2}{R^3} \right) [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)]. \quad (I.2)$$

Normally the needed integrals would be done by numerical methods. However, if the system is at high enough temperature such that $\left(\frac{C\mu_1\mu_2}{k_B T R^3} \right) \ll 1$, the exponential can be expanded in powers of the exponent, i.e.,

$$\exp[-\beta F(1, 2)] = 1 - \beta F(1, 2) + \frac{1}{2} [\beta F(1, 2)]^2 + \dots, \quad (I.3)$$

and the resultant integrals done by standard analytical methods.

Let us look first at the denominator of (I.1). We have:

$$\begin{aligned}
 &\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \exp[-\beta F(1, 2)] \\
 &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
 &\quad - \beta \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2)
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\beta^2}{2} \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 [F(1, 2)]^2 + \dots \\
& = A_1 - \beta A_2 + \frac{(\beta)^2}{2} A_3 + \dots
\end{aligned} \tag{I.4}$$

Then

$$\begin{aligned}
A_1 & = \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2; \\
& = [-\cos(\theta_1)]_0^\pi (2\pi) [-\cos(\theta_2)]_0^\pi (2\pi) \\
& = 2(2\pi) 2(2\pi) = (4\pi)^2
\end{aligned} \tag{I.5}$$

and

$$\begin{aligned}
A_2 & = \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2) \\
& = -\left(\frac{C\mu_1\mu_2}{R^3}\right) \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
& \quad \times [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)] = 0.
\end{aligned} \tag{I.6}$$

To convince ourselves that $A_2 = 0$, all we need to notice is that the following two integrals are vanishing. That is,

$$\begin{aligned}
& 2 \int_0^\pi \sin(\theta_1) \cos(\theta_1) d\theta_1 \\
& = \int_0^\pi \sin(2\theta_1) d\theta_1 = -\left[\frac{\cos(2\theta_1)}{2}\right]_0^\pi = -\left[\frac{1-1}{2}\right] = 0
\end{aligned} \tag{I.7}$$

and

$$\begin{aligned}
& \int_0^{2\pi} \cos(\phi_1 - \phi_2) d\phi_1 \\
& = \cos(\phi_2) \int_0^{2\pi} \cos(\phi_1) d\phi_1 + \sin(\phi_2) \int_0^{2\pi} \sin(\phi_1) d\phi_1 \\
& = \cos(\phi_2) [\sin(\phi_1)]_0^{2\pi} - \sin(\phi_2) [\cos(\phi_1)]_0^{2\pi} \\
& = \cos(\phi_2) [0 - 0] - \sin(\phi_2) [1 - 1] = 0.
\end{aligned} \tag{I.8}$$

The calculation of A_3 requires a little more effort. We have

$$\begin{aligned}
 \frac{A_3}{\left[-\left(\frac{C\mu_1\mu_2}{R^3}\right)\right]^2} &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \left[\frac{F(1, 2)}{-\left(\frac{C\mu_1\mu_2}{R^3}\right)} \right]^2 \\
 &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
 &\quad \times [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)]^2 \\
 &\equiv \text{Part}_1 + \text{Part}_2, \tag{I.9}
 \end{aligned}$$

where

$$\begin{aligned}
 \text{Part}_1 &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
 &\quad \times [4 \cos^2 \theta_1 \cos^2 \theta_2 + \sin^2 \theta_1 \sin^2 \theta_2 \cos(\phi_1 - \phi_2)^2]; \\
 \text{Part}_2 &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
 &\quad \times [-4 \cos \theta_1 \cos \theta_2 \cdot \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)] \\
 &= 0. \tag{I.10}
 \end{aligned}$$

We have asserted in the above that $Part_2$ is vanishing. This is assured by the fact that one of its multiplying factors is the integral $\int_0^{2\pi} \cos(\phi_1 - \phi_2) d\phi_1$. That integral was shown, in (I.8), to be equal to zero.

Regarding $Part_1$, it is convenient to separate it into two subsidiary parts. That is,

$$\text{Part}_1 \equiv \text{Part}_1(I) + \text{Part}_1(II) \tag{I.11}$$

where

$$\begin{aligned}
 \text{Part}_1(I) &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 [4 \cos^2 \theta_1 \cos^2 \theta_2] \\
 &= 4 \int_{\cos(\theta_1)=1}^{\cos(\theta_1)=-1} \cos^2 \theta_1 \{-d \cos(\theta_1)\} \int_0^{2\pi} d\phi_1 \\
 &\quad \times \int_{\cos(\theta_2)=1}^{\cos(\theta_2)=-1} \cos^2 \theta_2 \{-d \cos(\theta_2)\} \int_0^{2\pi} d\phi_2 \\
 &= 4 \int_{-1}^1 \eta^2 d\eta (2\pi) \times \int_{-1}^1 \gamma^2 d\gamma (2\pi) = 4 \left(\frac{4\pi}{3}\right)^2, \tag{I.12}
 \end{aligned}$$

and

$$\begin{aligned}
 \text{Part}_1(\text{II}) &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\
 &\quad \times \left[\sin^2 \theta_1 \sin^2 \theta_2 \cos(\phi_1 - \phi_2)^2 \right] \\
 &= \int_0^\pi \sin(\theta_1)^3 d\theta_1 \int_0^\pi \sin(\theta_2)^3 d\theta_2 \\
 &\quad \times \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \cos(\phi_1 - \phi_2)^2. \tag{I.13}
 \end{aligned}$$

Relevant integrals in (I.13) are done as follows:

$$\begin{aligned}
 \int_0^\pi \sin(\theta_1)^3 d\theta_1 &= \int_0^\pi \sin(\theta_2)^3 d\theta_2 = \int_0^\pi \left[\frac{3 \sin(\theta_1) - \sin(3\theta_1)}{4} \right] d\theta_1 \\
 &= \frac{3}{4} [1 + 1] - \frac{1}{4} \frac{[1 + 1]}{3} = \left(\frac{4}{3} \right); \\
 &\quad \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \cos(\phi_1 - \phi_2)^2 \\
 &= \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 [\cos(\phi_1)^2 \cos(\phi_2)^2 + \sin(\phi_1)^2 \sin(\phi_2)^2] \\
 &\quad + 2 \int_0^{2\pi} \sin(\phi_1) \cos(\phi_1) d\phi_1 \int_0^{2\pi} \sin(\phi_2) \cos(\phi_2) d\phi_2. \tag{I.14}
 \end{aligned}$$

The integrals in the last row in (I.14) are clearly both equal to zero. And the relevant integrals in the row before are of the form:

$$\begin{aligned}
 \int_0^{2\pi} d\phi_1 \cos(\phi_1)^2 &= \int_0^{2\pi} \left[\frac{1 + \cos(2\phi_1)}{2} \right] d\phi_1 = \left(\frac{2\pi}{2} \right); \\
 \int_0^{2\pi} d\phi_1 \sin(\phi_1)^2 &= \int_0^{2\pi} \left[\frac{1 - \cos(2\phi_1)}{2} \right] d\phi_1 = \left(\frac{2\pi}{2} \right).
 \end{aligned}$$

As a result

$$\begin{aligned}
 &\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \cos(\phi_1 - \phi_2)^2 \\
 &= \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 [\cos(\phi_1)^2 \cos(\phi_2)^2 + \sin(\phi_1)^2 \sin(\phi_2)^2]
 \end{aligned}$$

$$\begin{aligned}
 &+ 2 \int_0^{2\pi} \sin(\phi_1) \cos(\phi_1) d\phi_1 \int_0^{2\pi} \sin(\phi_2) \cos(\phi_2) d\phi_2 \\
 &= \left(\frac{2\pi}{2}\right)^2 + \left(\frac{2\pi}{2}\right)^2 + 2 \times 0 \times 0 = 2\pi^2.
 \end{aligned}
 \tag{I.15}$$

Combining (I.13)–(I.15) gives

$$\text{Part}_1(\text{II}) = \left(\frac{4}{3}\right) \times \left(\frac{4}{3}\right) \times (2\pi^2).$$

Having calculated $\text{Part}_1(I)$ and $\text{Part}_1(II)$ and recalling that Part_2 is vanishing – see (I.10) – we are now able to write the complete result for (I.4), namely the denominator of (I.1). Note this denominator is needed for the calculation of, u , the average energy per mole.

$$\begin{aligned}
 &\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \exp[-\beta F(1, 2)] \\
 &= A_1 - \beta A_2 + \frac{(\beta)^2}{2} A_3 + \dots \\
 &= (4\pi)^2 + 0 + \frac{\beta^2}{2} \left[\left(\frac{C\mu_1\mu_2}{R^3} \right) \right]^2 [\text{Part}_1(\text{I}) + \text{Part}_1(\text{II}) + \text{Part}_2] + \dots \\
 &= (4\pi)^2 + \frac{\beta^2}{2} \left[\left(\frac{C\mu_1\mu_2}{R^3} \right) \right]^2 \left[4 \left(\frac{4\pi}{3} \right)^2 + \left(\frac{4}{3} \right) \left(\frac{4}{3} \right) 2\pi^2 + 0 \right] + \dots \\
 &= (4\pi)^2 \left[1 + \frac{\beta^2}{3} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2 \right] + \dots
 \end{aligned}
 \tag{I.16}$$

Having thus calculated the denominator on the right hand side of (I.10, we deal next with the numerator. Expanding the exponential as given in (I.3), the numerator of (I.1) is the following:

$$\begin{aligned}
 &\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2) \exp[-\beta F(1, 2)] \\
 &= \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2) \\
 &\quad - \beta \int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 [F(1, 2)]^2 + \dots \\
 &= 0 - \beta A_3 \\
 &= -\beta \frac{2}{3} (4\pi)^2 \left[\frac{C\mu_1\mu_2}{R^3} \right]^2.
 \end{aligned}
 \tag{I.17}$$

Here, we have made use of the following information: As was demonstrated earlier – see (I.6) and the discussion that followed – we have

$$\int_0^\pi \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 F(1, 2) = 0.$$

Also, the last integral in (I.17) has already been evaluated as A_3 – see (I.4)–(I.16).

The average value, U , of the energy of N dipole pairs is N times the average energy, u , of a single dipole pair. Note that u is the ratio of the results given in (I.17) and (I.16). That is,

$$\begin{aligned} U &= Nu = \frac{-N\beta A_3}{(4\pi)^2 \left[1 + \frac{\beta^2}{3} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2 \right]} + \dots \\ &= -N\beta \frac{2}{3} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2 \left[1 - \frac{\beta^2}{3} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2 \right] + \dots \\ &\approx -N\beta \frac{2}{3} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2. \end{aligned} \quad (\text{I.18})$$

I.0.5 Average Force Between a Pair

The force Λ between any pair of dipoles can be determined by differentiating their intra-pair potential energy $F(1, 2)$ that was specified in (I.2). That is,

$$\begin{aligned} F(1, 2) &= - \left(\frac{C\mu_1\mu_2}{R^3} \right) [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)], \\ \Lambda &= - \left(\frac{\partial F(1, 2)}{\partial R} \right)_{\mu_1, \mu_2, \theta_1, \theta_2, \phi_1, \phi_2} = \left(\frac{3}{R} \right) F(1, 2). \end{aligned} \quad (\text{I.19})$$

Similar to the average energy of a pair, $\langle F(1, 2) \rangle$ – see (11.83) and (11.84) – we can also represent the average value of the intra-dipolar force, Λ , as $\langle \Lambda \rangle$. Very conveniently, in this case they are related!

$$\begin{aligned} \langle \Lambda \rangle &= \left(\frac{3}{R} \right) \langle F(1, 2) \rangle = \left(\frac{3}{RN} \right) U \\ &= -\beta \frac{2}{R} \left(\frac{C\mu_1\mu_2}{R^3} \right)^2. \end{aligned} \quad (\text{I.20})$$

(Note, U is as given in (I.18).)

Clearly, the thermodynamic average of the force between any single pair of dipoles is attractive.

Appendix J

Indistinguishable, Non-Interacting Quantum Particles

For a gas of n non-interacting free particles with mass m and momenta p , the Hamiltonian \mathcal{H}_n is

$$\mathcal{H}_n = \sum_p n_p \varepsilon_p, \tag{J.1}$$

where n_p is the number of free quantum particles with momentum p .

$$n = \sum_p n_p; \quad \varepsilon_p = \frac{p^2}{2m}. \tag{J.2}$$

Therefore, the partition function, given in (11.207), can be written as

$$\begin{aligned} \Psi(z, V, T) &= \sum_{n=0}^{\infty} \text{Tr} [\exp \{-\beta(\mathcal{H}_n - \mu n)\}] \\ &= \sum_{n=0}^{\infty} \text{Tr} \left[\exp \left\{ -\beta \left(\sum_p (\varepsilon_p - \mu) n_p \right) \right\} \right] \\ &= \sum_{n=0}^{\infty} \sum_{n_p}^{\prime} \prod_p [\exp \{-\beta (\varepsilon_p - \mu) n_p\}], \end{aligned} \tag{J.3}$$

where the primed sum over n_p , i.e., $\sum_{n_p}^{\prime}$, includes only those values of n_p for which $\sum_p n_p = n$.

Note: in deference to the physical requirements of the grand Canonical ensemble, the double summation in the last row of (J.3) must occur in the following manner:

First: we must sum over n_p in such a way that the total number of atoms are kept equal to n : that is, $\sum_p n_p = n$.

Second: the next summation is over n , which must include all physically allowed values.

An important mathematical result is that such double summation – in which the summation over n occurs after the n_p summation – is in fact equivalent to a product of independent, single sums over all values of the numbers n_p – and not just those that satisfy the sum-rule:¹ $\sum_p n_p = n$. As a result we can re-express the last row of (J.3) as follows:

$$\begin{aligned} \Psi(z, V, T) &= \sum_{n_o=0}^{n_{\max}} [\exp \{-\beta(\varepsilon_o - \mu)n_o\}] \\ &\times \sum_{n_1=0}^{n_{\max}} [\exp \{-\beta(\varepsilon_1 - \mu)n_1\}] \times \sum_{n_2=0}^{n_{\max}} [\exp \{-\beta(\varepsilon_2 - \mu)n_2\}] \times \cdots \quad (\text{J.4}) \end{aligned}$$

For the Bose–Einstein gas, n_{\max} can be as large as ∞ . On the other hand, for a Fermi–Dirac gas, the occupancy of each state is limited to two. Therefore, for an FD gas, n_o, n_1, n_2, \dots , etc., may take on only two values: 0 and 1.

J.1 Quantum Statistics: Grand Canonical Partition Function

The so called Bose–Einstein (BE) particles obey the Bose statistics in which there is no restriction on the occupation number of any state: so it can range between zero and infinity. Therefore, $n_{\max} = \infty$ and any of the sums in (J.4) – e.g., the i -th – can be written as follows:

$$\sum_{n_i=0}^{n_{\max}=\infty} [\exp \{-\beta(\varepsilon_i - \mu)n_i\}] = \left(\frac{1}{1 - \exp \{-\beta(\varepsilon_i - \mu)\}} \right). \quad (\text{J.5})$$

As a result, (J.4) becomes

$$\begin{aligned} [\Psi(z, V, T)]_{B-E} &= \Psi(z, V, T) \\ &= \prod_i \left(\frac{1}{1 - \exp \{-\beta(\varepsilon_i - \mu)\}} \right); \\ [Q(z, V, T)]_{B-E} &= \Delta_{B-E} \ln [\Psi(z, V, T)]_{B-E} \\ &= -\Delta_{B-E} \sum_i \ln [1 - \exp \{-\beta(\varepsilon_i - \mu)\}] \\ &= -\Delta_{B-E} \sum_i \ln [1 - z \exp (-\beta\varepsilon_i)]. \quad (\text{J.6}) \end{aligned}$$

¹A motivated student would want to test this assertion by working through the sum over n from $n = 0 \rightarrow 2$.

Recall that $z = \exp(\beta\mu)$. Also that Δ_{B-E} is the spin degeneracy weight factor which is equal to unity for the BE gas. Both ε_i and the sum \sum_i are explained in (J.9).

In contrast with Bose statistics, for Fermi particles with spin $\frac{1}{2}$, the sum over n_i is restricted to only two cases: $n_i = 0$ and 1 . This limits n_{\max} to the number 1 . Therefore, for the so called Fermi–Dirac(FD) gas, any of the sums in (J.4) – say, the i -th – can be written as:

$$\sum_{n_i=0}^{n_{\max}=1} [\exp\{-\beta(\varepsilon_i - \mu)n_i\}] = 1 + \exp\{-\beta(\varepsilon_i - \mu)\}. \quad (\text{J.7})$$

As a result (J.4) becomes

$$\begin{aligned} [\Psi(z, V, T)]_{F-D} &= \Psi(z, V, T) \\ &= \prod_i (1 + \exp\{-\beta(\varepsilon_i - \mu)\}); \\ [Q(z, V, T)]_{F-D} &= \Delta_{F-D} \ln [\Psi(z, V, T)]_{F-D} \\ &= \Delta_{F-D} \sum_i \ln [1 + \exp\{-\beta(\varepsilon_i - \mu)\}] \\ &= \Delta_{F-D} \sum_i \ln [1 + z \exp(-\beta \varepsilon_i)], \end{aligned} \quad (\text{J.8})$$

where the spin-degeneracy factor $\Delta_{F-D} = 2$.

Following a suggestion by Pathria, we can combine (J.6) and (J.8) and thus describe in a single equation the quantum non-interacting particles of both the BE and the FD varieties. While we do not necessarily need it, such description also simultaneously contains the corresponding representation for a classical non-interacting gas.

$$\begin{aligned} Q(z, V, T) &= \frac{\Delta}{a} \sum_i \ln [1 + a z \exp(-\beta \varepsilon_i)], \\ &\text{where} \\ a &= -1, \text{ for BE gas} \\ &= +1, \text{ for FD gas} \\ &\rightarrow 0, \text{ for classical gas,} \\ &\text{and} \\ \Delta &= (2S + 1) = 2, \text{ for spin } \frac{1}{2} \text{ FD gas} \\ &= 1, \text{ otherwise.} \end{aligned} \quad (\text{J.9})$$

Appendix K

Landau Diamagnetism

In addition to usual paramagnetism, conduction electrons are also subject to a sort of negative paramagnetism whereby the effect of applied field in a given direction produces a magnetic moment that faces in the opposite direction. Such behavior, resulting in negative susceptibility, is called: “diamagnetic.”

So far in our study of the conduction electrons, we have not considered any effects of the orbital motion. In the presence of applied magnetic field B_o – say, along the z-axis – an electron follows a helical path around the z-axis. The rotational motion is caused by the so called Lorentz force. Its projection on the x–y plane is completely circular. While a single rotating electron may be diamagnetic, when a large number N of electrons are present, and they are subject to reflection from the enclosing walls, classical statistics predicts that there is “complete” – i.e., to the leading order in N – cancelation of diamagnetic effect. Therefore, as first noted by Bohr, van Leeuwen, and others, classical statistical description of this motion cannot lead to diamagnetism.

Unlike classical statistics, L. D. Landau has shown that quantum statistics do lead to non-zero diamagnetism. While the details of Landau’s work are somewhat involved, a relatively simple general comment can still be made. Due to reflection from the bounding walls, the quantum electrons near the boundary – unlike the classical, Maxwell-Boltzmann electrons – have on the average different quantized velocities from the electrons that have not been reflected. Therefore, complete compensation of the diamagnetic effect that occurs for perfectly reflecting classical electrons does not take place for quantum electrons.

K.1 Analysis

For the electrons being studied, we assume there is no inter-particle interaction. Therefore, we can work with a collection of separate single particles.

A particle’s circular motion – say, with angular velocity ω – is quantized so that the relevant rotational energy levels are not continuous but are equal, say, to

$[\ell + (\frac{1}{2})](\hbar\omega)$, where $\ell=0,1,2,3,\dots$ (Here $\omega = (\frac{eB_o}{mc})$, e is the electronic charge, m its mass, and c is the velocity of light in vacuum.) While the energy for the longitudinal motion, i.e., $(\frac{p_z^2}{2m})$, is also quantized, due to the large size of the system the levels lie very close together. As a result, quantization along the z -direction can be ignored and p_z can be treated as a continuous variable. Therefore, the energy spectrum to treat is:

$$\begin{aligned}\epsilon &= \left[\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right] = \left[\ell + \left(\frac{1}{2} \right) \right] (\hbar\omega) + \left[\frac{p_z^2}{2m} \right] \\ &= \left[\ell + \left(\frac{1}{2} \right) \right] \left(\frac{\hbar e B_o}{mc} \right) + \left[\frac{p_z^2}{2m} \right] = -B_o \hat{M}_l + \left[\frac{p_z^2}{2m} \right].\end{aligned}\quad (\text{K.1})$$

Much as was done in (11.234), we work out the grand potential

$$Q(z, V, T, B_o) = \sum_{\epsilon} \ln \{1 + z \exp(-\beta\epsilon)\}.\quad (\text{K.2})$$

Then the total magnetic moment, M , is

$$M = \sum_{l=0}^N \langle \hat{M}_l \rangle = \frac{1}{\beta} \left(\frac{\partial Q(z, V, T, B_o)}{\partial B_o} \right)_{z, V, T}.\quad (\text{K.3})$$

Also, as noted in (11.237), the observed value of the number of particles \bar{N} is

$$\bar{N} = z \left(\frac{\partial Q(z, V, T, B_o)}{\partial z} \right)_{B_o, V, T}.\quad (\text{K.4})$$

K.1.1 Multiplicity Factor

We consider separately the contribution due to the rotational and the translational states. The first part of the integral then leads to the ‘‘multiplicity factor.’’

The quantized, rotational energy levels of a particle, that refer to the $x - y$ space, are necessarily degenerate due to the ‘‘coalescing together’’ of the almost continuous set of zero-field levels. As a result, essentially all those levels, that lie between any nearest two eigenvalues of the $x - y$ component of the Hamiltonian, coalesce together into a single level that may be characterized by the quantum index ℓ . The difference in energy between any nearest pair of levels is therefore independent of their quantum index ℓ . The number of these levels is the ‘‘multiplicity

factor.” According to Pathria¹ this factor is the: “quantum-mechanical measure of the freedom available to the particle for the center of its orbit to be ‘located’ in the total area XY of the physical space.” (In the present notation, the x - and the y -components of the total physical space are denoted as X and Y , respectively.) Pathria tells us that the multiplicity factor may be found to be the following:

$$\begin{aligned} & \left(\frac{XY}{h^2} \right) \times \left\{ \text{relevant area} : \int dp_x \int dp_y \right\} \\ &= \left(\frac{XY}{h^2} \right) 2\pi (m\hbar\omega) = XY \left(\frac{eB_o}{hc} \right). \end{aligned} \quad (\text{K.5})$$

As a result the grand potential—see, (K.1) and (K.2) — is:

$$\begin{aligned} Q(z, V, T, B_o) &= \sum_{\epsilon} \ln \{1 + z \exp(-\beta\epsilon)\} \\ &= XY \left(\frac{eB_o}{hc} \right) \sum_{\ell=0}^{\infty} \int_{-\infty}^{+\infty} \left(\frac{Z}{h} \right) dp_z \ln \{1 + z \exp(-\beta\epsilon)\} \\ &= \left(\frac{eVB_o}{h^2c} \right) \sum_{\ell=0}^{\infty} \int_{-\infty}^{+\infty} dp_z \\ &\quad \times \ln \left\{ 1 + z \exp \left[-\beta \left(\left[\ell + \left(\frac{1}{2} \right) \right] \left(\frac{\hbar e B_o}{m c} \right) + \left[\frac{p_z^2}{2m} \right] \right) \right] \right\}, \end{aligned} \quad (\text{K.6})$$

where we have replaced (XYZ) by the system volume V . At general temperatures, the integral above is best done numerically. However, in the limit of high and low temperature, it readily yields to analytical evaluation.

K.1.1.1 High Temperature

Here z and therefore $[z \exp(-\beta\epsilon)]$ are small compared to unity. Therefore

$$\ln \{1 + z \exp(-\beta\epsilon)\} = z \exp(-\beta\epsilon) + O [z \exp(-\beta\epsilon)]^2. \quad (\text{K.7})$$

Accordingly, at high temperatures, (K.6), (K.4) and (K.3) lead to the following results for the grand potential, average number of particles, and the total diamagnetic moment.

¹See Pathria’s equation (8.2.29). op. cit.

$$\begin{aligned}
Q(z, V, T, B_o) &\approx \left(\frac{eVB_o}{h^2c} \right) z \int_{-\infty}^{+\infty} \exp \left(-\frac{\beta p_z^2}{2m} \right) dp_z \\
&\times \sum_{\ell=0}^{\infty} \exp \left\{ -\beta \left[\ell + \left(\frac{1}{2} \right) \right] (\hbar\omega) \right\} \\
&= \left(\frac{zeVB_o}{2h^2c} \right) (2\pi m k_B T)^{\frac{1}{2}} \left\{ \sinh \left(\frac{\beta \hbar e B_o}{2mc} \right) \right\}^{-1}. \quad (\text{K.8})
\end{aligned}$$

In (K.8) above, use was made of the following identity:

$$\begin{aligned}
\sum_{\ell=0}^{\infty} \exp \left\{ -\beta \left[\ell + \left(\frac{1}{2} \right) \right] (\hbar\omega) \right\} &= \left(\frac{\exp \left\{ -\beta \left(\frac{\hbar\omega}{2} \right) \right\}}{1 - \exp \left\{ -\beta (\hbar\omega) \right\}} \right) \\
&= \left\{ 2 \sinh \left(\frac{\beta \hbar\omega}{2} \right) \right\}^{-1}. \quad (\text{K.9})
\end{aligned}$$

Also, ω was replaced by its value $\left(\frac{eB_o}{mc} \right)$.

In order to determine the diamagnetic susceptibility per particle, we need to find the total magnetization as a function of the applied field and the measured value \bar{N} – namely, the thermodynamic average – of the number of particles present. The latter, according to (K.4), involves differentiation with respect to z and then multiplication by z . Similarly, the high temperature result for the Landau diamagnetic moment, $(M)_{\text{landau}}$, can be found from (K.3) and (K.8). In this manner, we readily find:

$$\begin{aligned}
\bar{N} &= z \left(\frac{\partial Q(z, V, T, B_o)}{\partial z} \right)_{V, T, B_o} = Q(z, V, T, B_o); \\
(M)_{\text{landau}} &= \frac{1}{\bar{N} \beta} \left(\frac{\partial Q(z, V, T, B_o)}{\partial B_o} \right)_{z, V, T} \\
&= \left(\frac{1}{\beta B_o} \right) \left\{ 1 - \left(\frac{\beta \hbar e B_o}{2mc} \right) \coth \left(\frac{\beta \hbar e B_o}{2mc} \right) \right\} \\
&= - \left(\frac{e \hbar}{2mc} \right) \left[\coth \left(\frac{\beta \hbar e B_o}{2mc} \right) - \left(\frac{2mc}{\beta \hbar e B_o} \right) \right] \\
&= -\mu_B L(\Upsilon), \quad (\text{K.10})
\end{aligned}$$

where $\mu_B = \left(\frac{e \hbar}{2mc} \right)$ is the Bohr magneton and

$$\begin{aligned}
\Upsilon &= \left(\frac{\beta \hbar e B_o}{2mc} \right) = (\beta B_o \mu_B); \\
L(\Upsilon) &= [\coth(\Upsilon) - (1/\Upsilon)]. \quad (\text{K.11})
\end{aligned}$$

At high temperatures, unless the applied field, B_o , is exceptionally large, $\Upsilon \ll 1$. As a result $L(\Upsilon) = (\Upsilon/3) - O[(\Upsilon)^3]$, and the thermodynamic average of the diamagnetic moment per particle and the resultant Landau susceptibility, $(\chi)_{\text{landau}}$, are as follows:

$$\begin{aligned} (M)_{\text{landau}} &= -\left(\frac{B_o \mu_B^2}{3k_B T}\right) + O[\mu_B (\beta B_o \mu_B)^3]; \\ (\chi)_{\text{landau}} &= \frac{(M)_{\text{landau}}}{B_o} = -\left(\frac{\mu_B^2}{3k_B T}\right). \end{aligned} \quad (\text{K.12})$$

Except for the negative sign, other features of this result are reminiscent of those of Langevin's classical theory result for paramagnetism! [For example, compare (11.98) where we found: $(\chi)_{\text{Langevin classical}} = \mu_c^2/(3k_B T)$. Recall that μ_c was the magnetic moment of a single Langevin-particle.] We hasten to add, however, that this is merely an happenstance and has no fundamental significance (that, at least the current author is aware of).

At such high temperature, the Pauli result for the paramagnetic susceptibility of a gas of free, quantum electrons appears to be equal to the corresponding quasi-classical estimate given in (11.296). The equality holds only when the Lande g factor is equal to 2. Then we can legitimately replace the "intrinsic magnetic moment per electron," $(\frac{g\mu_B}{2})$, by the Bohr magneton μ_B .

Adding that result to Landau diamagnetism yields

$$\begin{aligned} \chi_{\text{electron at high temperature}} &= (\chi)_{\text{quasi-classical}} + (\chi)_{\text{landau}} \\ &= \left(\frac{\mu_B^2}{k_B T}\right) - \left(\frac{\mu_B^2}{3k_B T}\right), \end{aligned} \quad (\text{K.13})$$

Observe that we have not used the obvious simplification – namely, $(\frac{2\mu_B^2}{3k_B T})$ – for the sum of the above two terms. The reason is that depending upon the source of the free electrons being considered, μ_B occurring in the two terms in the above equation may be slightly different. This is because of its dependence on the effective electronic mass and/or the Lande g -factor, which are not necessarily the same for the two processes being represented.

Appendix L

Specific Heat for the BE Gas

Knowing the internal energy in the form of (11.365), that is $U = \frac{3}{2} N k_B T \left[\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \right]$, the objective of the present appendix is to derive the general expression for the specific heat that is given in (11.366).

L.1 Analysis

Briefly we proceed as follows: First, we determine the derivative of $g_n(z)$.

$$\begin{aligned}
 z \left(\frac{\partial g_n(z)}{\partial z} \right)_V &= \frac{z}{\Gamma(n)} \int_0^\infty \exp(x) x^{n-1} [\exp(x) - z]^{-2} dx \\
 &= \frac{z}{\Gamma(n)} \left[-\frac{x^{n-1}}{\exp(x) - z} \Big|_0^\infty \right] \\
 &\quad + \frac{z(n-1)}{\Gamma(n)} \left[\int_0^\infty x^{n-2} [\exp(x) - z]^{-1} dx \right] \\
 &= 0 + \frac{1}{\Gamma(n-1)} \int_0^\infty x^{n-2} [z^{-1} \exp(x) - 1]^{-1} dx \\
 &= g_{n-1}(z).
 \end{aligned} \tag{L.1}$$

(Note that here V is just a dummy index.) Then we write:

$$\frac{C_v(T)}{N k_B} = \frac{1}{N k_B} \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} \left[\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \right]$$

$$+ \left(\frac{3T}{2g_{\frac{3}{2}}^2(z)} \right) \left[g_{\frac{3}{2}}(z) \left(\frac{\partial g_{\frac{5}{2}}(z)}{\partial z} \right)_V - g_{\frac{5}{2}}(z) \left(\frac{\partial g_{\frac{3}{2}}(z)}{\partial z} \right)_V \right] \left(\frac{\partial z}{\partial T} \right)_V. \quad (\text{L.2})$$

Next, we need to determine $\left(\frac{\partial z}{\partial T} \right)_V$. To this purpose we begin with (11.363): namely

$$g_{\frac{3}{2}}(z) = \left(\frac{N}{V} \right) \lambda^3,$$

where, as always,

$$\lambda = \left(\frac{2\pi m k_B T}{h^2} \right)^{-\frac{1}{2}}. \quad (\text{L.3})$$

Then

$$\begin{aligned} \left(\frac{\partial g_{\frac{3}{2}}(z)}{\partial T} \right)_V &= \left(\frac{\partial g_{\frac{3}{2}}(z)}{\partial z} \right)_V \left(\frac{\partial z}{\partial T} \right)_V = \left[\frac{g_{\frac{1}{2}}(z)}{z} \right] \left(\frac{\partial z}{\partial T} \right)_V \\ &= \left(\frac{-3N}{2TV} \right) \lambda^3 = \left(-\frac{3}{2T} \right) g_{\frac{3}{2}}(z), \end{aligned} \quad (\text{L.4})$$

which leads to

$$\left(\frac{\partial z}{\partial T} \right)_V = - \left(\frac{3z}{2T} \right) \frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)}. \quad (\text{L.5})$$

Now we insert $\left(\frac{\partial z}{\partial T} \right)_V$ given above into (L.2). This finally leads to the specific heat $C_v(T)$ that is valid for temperatures $T \geq T_c$.

$$C_v(T) = Nk_B \left[\frac{15}{4} \left(\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} \right) - \frac{9}{4} \left(\frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \right) \right]. \quad (\text{L.6})$$

Index

- 4.184000 Joules
 one-gram water/degree
 calorie, 59
- N_A , Avogadro's Number, 26
- N_A , Avogadro's number
 = 6.02214179(30)
 $\times 10^{23} \text{ mol}^{-1}$, 5
- $Q^{\text{rev}}(T_H)$, $Q^{\text{rev}}(T_C)$, 130
- $T.dS$
 first and second equations
 together, 234
 first equation, 215
 second equation, 231
 third equation, 235
- $T.dS$ Equation
 first, 215
 first and second
 together, 234
 second, 231
 third, 235
- $V_{\text{excluded}} =$
 $4N \left[\frac{4\pi}{3} (r_o)^3 \right]$, 257
- X_o versus p_o
 (6.91), 283, 285
- $\Delta S_{\text{total}}(\text{spontaneous}) > 0$, 144
- $\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial t} \right)_p$, 66
- $\alpha_p > 0$ means
 that system expands with
 increasing temperature, 216
- $\alpha_p > 0$ means also
 that $\alpha_s < 0$, 216
- $\alpha_s = \frac{1}{v} \left(\frac{\partial v}{\partial t} \right)_s$, 68
- $\chi_t = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_t$, 67
- $\left(\frac{\partial h}{\partial p} \right)_t - v = -t \left(\frac{\partial v}{\partial t} \right)_p$,
 alternate proof, 233
- $\left(\frac{\partial h}{\partial p} \right)_t - v = -t \left(\frac{\partial v}{\partial t} \right)_p$,
 proof, 230
- $\left(\frac{\partial u}{\partial v} \right)_t = t \left(\frac{\partial p}{\partial t} \right)_v - p$,
 proof, 214
- $\epsilon_{\text{max}} = \epsilon_{\text{carnot}}$, 380
- $\epsilon_{\text{Heat Energy Pump-Carnot}}$, 191
- $\epsilon_{\text{carnot}} = 1 - \left(\frac{T_C}{T_H} \right)$, 133
- $\frac{c_p}{c_v} \equiv \gamma$, 98
- $\gamma \equiv \frac{c_p}{c_v}$, 98
- $\left(\frac{dq^{\text{rev}}}{t} \right) = ds$, 213
- $\Delta_p = -tv\alpha_p$, 78
- $\Delta_v = t \left(\frac{\partial p}{\partial t} \right)_v = \frac{t\alpha_p}{\chi_t}$, 86
- c_v dependence on v , 217
- $c_v = -\left(\frac{tv\alpha_s\alpha_p}{\chi_t} \right)$, 79
- $c_v = \left(\frac{\partial u}{\partial t} \right)_v$, 65
- $c_p - c_v = \left(\frac{tv\alpha_p^2}{\chi_t} \right)$, 68
- $c_p - c_v$ as above by different rout, 85
- c_p dependence on p , 232
- $c_p - c_v = c_v(\gamma - 1) = R$, for monatomic
 ideal gas, 100
- $c_p = -\left(\frac{tv\alpha_s\alpha_p}{\chi_s} \right)$, 79
- $c_p = \left(\frac{\partial h}{\partial t} \right)_p$ where $h = u + pv$, 77
- k_B , Boltzmann Constant
 = 1.3806504(24) $\times 10^{-23}$
 $J K^{-1}$, 27
- p and v Independent, 235
- $t ds = c_p dt - tv\alpha_p dp$,
 second t.ds equation, 231
- $t ds = c_v dt + t \left(\frac{\alpha_p}{\chi_t} \right) dv$,
 first t.ds equation, 216

$$t ds = c_v \left(\frac{\chi_L}{\alpha_p} \right) dp + \left(\frac{c_p}{v\alpha_p} \right) dv,$$

third t.ds equation, 235

t and p Independent, 230

t and v Independent, 213

$$\left(\frac{\partial u}{\partial v} \right)_t = t \left(\frac{\partial p}{\partial t} \right)_v - p,$$

alternate proof, 218

dW

not exact differential, 60

'Jacobian determinant', 16

'Simple' System, 59

'Simple' system, 14

'a priori', 4

dW

quasi-static $\equiv P dV$, 59

Hess' Rules

chemo-thermal reactions, 82

Prove $\left(\frac{\partial t}{\partial v} \right)_h =$

$$\frac{1}{v} (\alpha_p - \frac{\chi_L}{\mu})^{-1}, 334$$

Adiabatic

enclosure, 2

walls, 2

Adiabatic Expansion

then isothermal compression

work done in ideal gas, 93

Adiabatic state equation

Van der Waals gas

above critical point, 297

above critical point $u, h, s, C_p - C_v$,

298

Adiabatically

enclosed system, 2

isolated system, 2

Adiabatics

for the Ideal Gas, 91

Adiabats, 131

Air Rapidly Let Out

of inflated tire, 216

Anharmonic Oscillators, xi

Argon, 264, 283

Atkins, Julio de Paula, 281

Atkins, Peter, 281

Atm = 760 Torr, 400

Atmosphere

energy of isothermal, 42

altitude below which given

percentage of molecules present, 41

barometric equation for

isothermal atmosphere, 38

water boiling under one

atmosphere of air, 32, 33

Attraction, long range

pressure change

Van der Waals gas, 257

Available Work

maximum, 380

Avogadro Number N_A , 27

Avogadro's number N_A

$$= 6.02214179(30)$$

$$\times 10^{23} \text{ mol}^{-1}, 5$$

Avogadro, Lorenzo Romano Amadeo Carlo

(8/9/1776)–(6/9/1856), 5

Back-of-the-Envelope

Van der Waals

gas subject to internal pressure, 319

Barometric Equation, 38

a related calculation, 40

for atmosphere with height dependent

temperature, 44

Behavior below T_c

Van der Waals, 269

Benjamin Thompson

Count Rumford of Bavaria, viii

Berthollet, Claude Louis

(12/9/1748)–(11/6/1822), 255

BMG \equiv

boltzmann–Maxwell–Gibbs, 26

BMG \equiv

postulate, 27

Boas, M. L.

mathematical methods

John Wiley, 17

Boltzmann Constant

$$k_B = 1.3806504(24) \times 10^{-23}$$

$$J K^{-1}, 27$$

$$k_B = \left(\frac{R}{N_A} \right), 35$$

Boltzmann, Ludwig Eduard

(2/20/1844)–(9/5/1906), 26

Boltzmann–Maxwell–Gibbs

(BMG) distribution, 26

Boyle, Robert

(1/25/1627)

–(12/31/1691), 31

Bromine, 265

Calculation

back of the envelope

Van der Waals gas subject to internal

pressure, 319

- Callen
 op. cit., 342
 remarks:
 equations of state, 342
 rule, 342
 rule, check
 in energy representation, 350
 scaling principle, 343
 scaling relation
 checked, 349
- Callen, Herbert B
 (1919)–(5/22/1993), xii
- Caloric Theory, 58
- Calorie
 thermochemical, 58
- Carbon
 dioxide, 265
 monoxide, 264
- Carbon-12
 atomic mass, 5
- Carnot, ix
 ϵ_{carnot}
 efficiency of engine, 133
 cycle, 130
 engine causes no change
 in entropy of universe, 166
 engine efficiency independent of working
 substance, 141
 engine with arbitrary working substance,
 139
 heat energy pump, 190
 ideal gas working substance, 128
 infinitesimal cycles, 136
 perfect engine, 128
 perfect engine \equiv engine, 128
 refrigerator or air-conditioner, 185
 second-law, statement, 141
 version of second law, 135
- Carnot cycles
 entropy and work, 159
- Carnot Violation
 leads to violation of Clausius
 and Kelvin-Planck, 145
- Carnot, N. L. Sadi
 (6/1/1796)
 -(8/24/1832), 31
- Celsius, Anders
 (11/27/1701)
 -(4/25/1744), 32
- Celsius, Anders
 temperature, 32
- Chain rule, 17
- Change of State
 isothermal-
 isochoric, 381
- Chapter
 VI, Van der Waals theory
 of imperfect gases, 255
 I, a thermodynamic system, 1
 II, perfect gas, 23
 III, first law, 57
 IV, second law, 125
 IX, zeroth law revisited
 thermodynamic stability motive forces,
 353
 V, first and
 second laws, 211
 VII, internal energy and enthalpy
 measurement and related examples, 303
 VIII, fundamental equation;
 equation of state, 337
 X, Legendre transformations
 thermodynamic potentials; Clausius–
 Clapeyron; Gibbs phase rule,
 373
- Chapter 1
 Zeroth law
 introduction and, 1
- Chapter VII
 internal energy and enthalpy:
 measurement and related examples, 303
- Characteristic Equations:
 Gibbs potential known, 393
 Helmholtz potential known, 392
- Charles, Jacques Alexander César
 (11/12/1746)
 -(4/7/1823), 32
- Chemical Potential, 338
- Chemo-Thermal Reaction, 88
- Chlorine, 265
- Clapeyron, Benoit Paul Emil
 (2/26/1799)
 -(1/28/1864), 373
- Clausius
 important consequence of statement, 142
 inequality, a statement
 of the second law, 152
 inequality, differential form, 151
 inequality, integral form, 148
 second law, 142
 statement leads
 to Kelvin-Planck, 145
 version of
 first-second law, 152, 212
- Clausius Inequality
 differential form, 380
- Clausius inequality
 differential form, 150

- integral form, 148
 - statement of second-law, 152
- Clausius Version
 - second law, 366
- Clausius, Rudolf Julius Emanuel
 - (1/2/1822)
 - (8/24/1888), 142
- Clausius–Clapeyron
 - differential equation, 397
 - differential equation, 396
 - solution, 399
 - phase boundaries, 398
- Clausius-Clapeyron
 - differential equation, x
- CO and CO₂, 89
- co-existent regime
 - reduced vapor pressure, 290
- Coefficient
 - isentropic compressibility, χ_s , 81
 - isentropic volume expansion α_s , 68
 - isobaric volume expansion α_p , 66
 - isothermal compressibility χ_t , 66
- Component
 - multiple, 341
 - single, 341
- Comprehension, better, vii
- Compressibility
 - χ_s , quasi-static adiabatic
 - ≡ isentropic, 81
 - χ_t , quasi-static isothermal, 81
- Compression
 - isothermal, 360
- Compression and Rarefaction, 237
- Conversion
 - heat energy into work, 62
 - work into heat energy, 62
- Cord
 - extended
 - entropy change, 248
- Corresponding states
 - principle of: *PCS*, 282
- Critical
 - constants P_c , V_c , T_c , 264
 - densities
 - difference in, 277
 - point, 262
 - region
 - Van der Waals gas, 265
 - temperature just below critical point, 277
- Critical point
 - temperature, just below, 277
- Cycle
 - Carnot, 130
 - perfect Carnot cycle
 - ≡ Carnot cycle, 128
- Cyclic identity, 14
 - re-derived, 19
- Dalton's Law
 - of partial pressures, 36
- Dalton's law of partial pressures
 - not necessarily valid for
 - Van der Waals mixtures, 260
- Dalton, John
 - (9/6/1766)–(7/27/1844), 37
 - (9/6/1766–7/27/1844), 260
- Degrees of Freedom
 - diatomic Gas, 35
- Dependence
 - c_p on p , 232
- Dependence of c_v on v , 217
- Dependence of c_p on p , 232
- Derivative
 - partial, 18
- Determinant, 18
- Diathermal, 98
 - walls, 2
- diathermal
 - wall, 359
- Diathermi
 - cas
 - heat flow, 357
- Diatomic, 92
- Diatoms, 34
- Diesel cycle, 199
- Dieterici
 - equation of state, 256
 - gas, behavior, 300
 - isotherms, 302
- Dieterici's equation of state, 300
- Differential
 - exact, 9, 12
 - inexact, 13
 - total, 9
- Dillio, Charles C., 282
 - with Nye, Edwin P.
 - thermal engineering, international text
 - book company(1963), 282
- Direction
 - of thermodynamic motive forces, 357
- Dittman, R. H.
 - 'Heat and Thermodynamics'
 - McGraw Hill(1981), 311
- Domb, Cyril
 - (12/9/1920), 258
- Duhem
 - Gibbs-Duhem relation

- energy representation, 345
- entropy representation, 345
- Efficiency
 - Carnot engine, 133
 - of Carnot engine, 132
- Elastic Moduli, 57
- Electromagnetic
 - field quanta, 1
- Empirical Temperature
 - to thermodynamic T , 322
- Empirical temperature, 5, 7
- Empirical to
 - thermodynamic
 - temperature, 31
- Energy
 - Carnot heat pump, 190
 - change in leaky container, 49
 - conservation, 61
 - extremum, 361
 - in the Perfect Gas, 28
 - of isothermal atmosphere, 42
 - representation, 343
 - Gibbs-Duhem relation, 345
 - ideal gas fundamental equation, 349
- Energy
 - representation
 - ideal gas three equations
 - of state, 349
- Energy and Entropy
 - extremum principles
 - are equivalent, 361
- Energy and Entropy Extrema
 - occur together, 361
- Energy Extremum
 - minimum energy, 361
- Energy Formalism
 - motive forces, 364
- Energy Representation, 343
 - Gibbs-Duhem relation, 345
 - ideal gas
 - fundamental equation, 349
 - three equations
 - of state, 349
- Engin
 - diesel, 199
- Engine
 - ideal gas
 - carnot engine, 128
 - perfect, Carnot, 128
 - realistic but
 - idealized, 199
- Enthalpy, 81
 - and internal energy
 - measurement and related examples, 303
 - and the first law
 - $dq = dh - vd p$, 83
 - characteristic independent
 - variables: p and s , 389
 - constant
 - Joule-Kelvin experiment, 308
 - curves of constant
 - \equiv isenthalpic, 311
 - gaseous cooling and
 - constant enthalpy curves, 310
 - heat of transformation and internal energy,
 - 86
 - remarks, 389
 - state function, 78, 82
- Enthalpy Minimu
 - from virial coefficients, 321
- Entropy, 136
 - always increases in
 - irreversible-adiabatic process, 146
 - compute via reversible paths, 138
 - increase in spontaneous process, 142
 - representation, 343
 - Gibbs-Duhem relation, 345
 - ideal gas fundamental relation, 346
 - ideal gas three equations
 - of state, 348
 - state function, 138
- Entropy and Energy
 - extremum principles
 - are equivalent, 361
- Entropy Change
 - mixing of ideal gas:
 - different temperature, pressure and
 - number of atoms, 225
 - isothermal, different pressures, 219
 - isothermal, different pressures and
 - number of atoms, 222
- Entropy Extremum
 - maximum entropy, 357
- Entropy Flow, Isobaric:
 - from higher temperature
 - region to lower temperature region, 364
- Entropy Maximum:
 - specific entropy is equal, 376
- Entropy Representation
 - Gibbs-Duhem relation, 345
 - ideal gas
 - fundamental relation, 346
 - three equations
 - of state, 348
- Equation
 - first $T.dS$, 215

- first and second together, 234
 - of state, 9
 - second $T.dS$, 231
 - third $T.dS$, 235
- Equation of State
 - Van der Waals for a mixture, 260
- Equation of State
 - from χ_t and α_p , 104, 106, 108, 109, 111, 112, 114, 116, 117, 119
 - construction from knowledge
 - of bulk and elastic moduli, 103
 - reduced form Van der Waals, 264
 - Van der Waals gas, 71
- Equation of state, 8
 - a definition, 30
 - Dieterici, 300
 - in reduced form, 260
 - perfect gas, 30
- Equations of State, 342
 - known for
 - the ideal gas, 344
 - third,
 - for the ideal gas, 344
 - three, for ideal gas
 - energy representation, 349
 - entropy representation, 348
- Equations of state, 8
- Equilibrium
 - meta-stable, 395
 - of different macroscopic parts, 31
 - thermal, 3
- Equivalence
 - energy and entropy extremum principles, 361
- Erg, 58
- Ethane, 265
- Ethylene, 265
- Euler Equation, ix
 - multiple-component systems, 341
 - single-component systems, 338
- Exact differential, 9
- Example
 - I, chapter VIII, 350
 - II, chapter VIII, 351
 - VI chap VII,
 - c_v , internal energy and volume dependence, 288
- Examples, 85
- Examples Chapter II
 - 1, partial pressure of mixtures, 47
 - 2, dissociating tri-atomic ozone, 48
 - 3, energy change in leaky container, 49
 - 4, mixture of carbon and oxygen, 50
 - 5, carbon on burning, 51
 - 6, pressure, volume and temperature, 52
 - 7, addition to example 6, 53
- Examples Chapter III
 - 1, heat energy needed for raising temperature, 68
 - 10, latent heat of vaporization of water, 90
 - 11, perfect gas adiabatic expansion then isothermal compression: work done, 92
 - 12, non-quasi-static free adiabatic expansion of ideal gas, 95
 - 13, quasi-static adiabatic compression of ideal gas, 96
 - 14, isobaric, isothermal, or adiabatic expansion of diatomic ideal gas, 96
 - 15, conducting and non-conducting cylinders in contact, 98
 - 16 to 21, some inter-relationships, 101
 - 16, alternate proof of:

$$c_v \left(\frac{\partial T}{\partial v} \right)_u = - \left(\frac{\partial u}{\partial v} \right)_T, 101$$
 - 17, proof of:

$$c_v \left(\frac{\partial T}{\partial p} \right)_v = \left(\frac{\partial u}{\partial p} \right)_v, 101$$
 - 18, proof of:

$$c_p \left(\frac{\partial T}{\partial v} \right)_p = \left(\frac{\partial h}{\partial v} \right)_p, 102$$
 - 19, proof of:

$$c_p = \left(\frac{\partial u}{\partial T} \right)_p + p v \alpha_p, 102$$
 - 2, change in pressure, volume, and temperature; work done and increase in U , 69
 - 20, proof of:

$$\left(\frac{\partial h}{\partial T} \right)_v = c_v + v \left(\frac{\alpha_p}{\chi_t} \right), 102$$
 - 21, proof of:

$$\left(\frac{\gamma}{v \chi_t} \right) = \left(\frac{\partial h}{\partial v} \right)_p \left(\frac{\partial p}{\partial u} \right)_v, 103$$
 - 22, equation of state from

$$\chi_t = \frac{R t v}{(v-b)^2} - \left(\frac{2a}{v^2} \right) \text{ and } \alpha_p = \frac{R \chi_t}{(v-d)}, 104$$
 - 23, alternate solution of example 22, 106
 - 24, equation of state from

$$\chi_t = \left(\frac{b}{v} \right) \text{ and } \alpha_p = \left(\frac{a t}{v} \right), 108$$
 - 25, equation of state from

$$\chi_t = a/(p^3 t^2) \text{ and } \alpha_p = b/(p^2 t^3), 109$$
 - 26, alternate solution of example 25, 111

- 27, equation of state after solving for χ_t and α_p , 112
- 28, equation of state from given χ_t and α_p , 114
- 29, alternate solution of example 28, 116
- 3, work done by expanding Van der Waals gas, 71
- 30, equation of state from $\chi_t^{-1} = (p + b)$ and $\alpha_p = \frac{R}{v(p+b)}$, 117
- 31, equation of state from constant χ and α , 119
- 32, related to Newton's law of cooling, 121
- 33, volume dependence of single particle energy levels, 122
- 4, work done and volume change metal versus gas, 72
- 5, equation of state from change in pressure and temperature, 73
- 6, spreading gas among three compartments, 74
- 7, $(c_p - c_v) = -\Delta_p \left(\frac{\partial p}{\partial t} \right)_v = \Delta_v \left(\frac{\partial v}{\partial t} \right)_p$, 85
- 8, internal energy from latent heat of vaporization, 86
- 9, oxidation of CO to CO₂, 89
- Examples Chapter IV
 - 1 to 3, entropy change and thermal contact, 153
 - 1, an object and a reservoir, 153
 - 10, between three finite masses, 171
 - 11, alternate solution of example 10, 172
 - 12, Carnot engine and three reservoirs, 174
 - 13, alternate solution of example 12, 176
 - 14, two masses and reservoir, 178
 - 15, alternate solution of example 14, 179
 - 16, Carnot engine two finite sources with temperature dependent specific heat, 183
 - 17, work needed for cooling object with constant specific heat, 187
 - 18, temperature dependent cooling, entropy change and work input, 188
- 19, entropy increase on removing temperature gradient, 192
- 2, two finite masses entropy change, 155
- 20, maximum work available in example 19, 195
- 21, diesel engine, 201
- 22, Joule engine, 208
- 3, reservoir and mass temperature-dependent, 157
- 4, changes along Carnot paths, 159
- 5, an object and reservoir, 161
- 6, alternate solution of example 5, 163
- 7, maximum work and entropy change, 167
- 8, between two finite masses, 168
- 9, alternate solution of example 8, 169
- Examples Chapter V
 - 1, mixing ideal gases isothermal, different pressures, same number of atoms, 219
 - 10, $\left(\frac{v}{c_p} \right) = \left(\frac{\partial t}{\partial p} \right)_s - \left(\frac{\partial t}{\partial p} \right)_h$, 243
 - 11, isothermally stretched ideal rubber, 244
 - 12, energy and entropy change in Van der Waals gas, 246
 - 13, equation of state of a metal rod, 247
 - 14, entropy change in extendable cord, 248
 - 15, Carnot Engine a 'trick' question, 250
 - 2, mixing ideal gases isothermal, different pressures, different number of atoms, entropy change, 221
 - 3, mixing ideal gases different temperature, different pressures, different number of atoms, entropy change, 225
 - 4, if $\left(\frac{p}{t} \right) = \left(\frac{\alpha_p}{\chi_t} \right)$ then $\left(\frac{\partial c_v}{\partial v} \right)_t = 0$, 228
 - 5, gas and reservoir change in u and s , 238
 - 6 and 7,

- $\Delta W, \Delta U, \Delta S$
calculations, 239
- 8, $\left(\frac{\chi_t}{\chi_s}\right) = 1 - \left(\frac{\alpha_p}{\alpha_s}\right)$, 241
- 9, $c_p \left(\frac{\partial t}{\partial s}\right)_h = t - \alpha_p t^2$, 242
- Examples Chapter VI
- 1, pressure versus volume
for critical isotherm Van der Waals, 267
 - 10, Van der Waals gases:
adiabatic equation of state above critical point, 297
 - 11, adiabatic state equation
and $u, h, s, c_p - c_v$, for given gas, 298
 - 12, behavior of
Dieterici gas, 300
 - 2, isothermal compressibility
along critical isochore just above T_c ,
268
 - 3, difference in
critical densities, 277
 - 4, saturation pressure, 279
 - 5, isothermal compressibility
just below T_c , 280
 - 6 to 9, 288
 - 6, internal energy and
volume dependence of c_v , 288
 - 7, Van der Waals gases:
temperature change on mixing, 290
 - 8, Van der Waals gases:
specific heats, enthalpy, η and μ , 293
 - 9, Van der Waals gases:
work done, internal energy and entropy
change, 296
- Examples Chapter VII
- 1, Gay-Lussac-Joule
coefficient for perfect gas, 306
 - 10, Prove $\left(\frac{\partial t}{\partial p}\right)_h - \left(\frac{\partial t}{\partial p}\right)_s$
 $= -\left(\frac{v}{C_p}\right)$, 331
 - 11, Prove $\left(\frac{v\chi_t}{\mu}\right) \left(\frac{\partial h}{\partial v}\right)_t$
 $= c_p$, 332
 - 12, Prove $\frac{1}{\eta v \chi_t} \left(\frac{\partial u}{\partial p}\right)_t$
 $= c_v$, 333
 - 13, Prove $\left(\frac{\partial h}{\partial t}\right)_v$
 $= c_p(1 - \mu \alpha_p / \chi_t)$, 333
 - 14, Prove $\left(\frac{\partial t}{\partial v}\right)_h$
 $= \frac{1}{v}(\alpha_p - \frac{\chi_t}{\mu})^{-1}$, 334
 - 15, Prove $\left(\frac{\partial u}{\partial s}\right)_v = t$
and $\left(\frac{\partial u}{\partial v}\right)_s = -p$, 335
 - 2, Gay-Lussac-Joule
coefficient for nearly perfect gas, 306
 - 3, Gay-Lussac-Joule
coefficient for Van der Waals gas, 307
 - 4, Joule-Kelvin coefficient
for perfect gas, 313
 - 5, Joule-Kelvin coefficient
for nearly perfect gas, 313
 - 6, Van der Waals Gas
adiabatic-free expansion, 318
 - 7, hydrogen gas
estimated inversion pressure from state
equation, 320
 - 8, enthalpy minimum
for gas with known three virial
coefficients, 321
 - 9, Prove $\left(\frac{\partial t}{\partial v}\right)_u - \left(\frac{\partial t}{\partial v}\right)_s$
 $= \left(\frac{p}{C_v}\right)$, 330
alternate solution
of example 7, 320
- Examples Chapter VIII
- 1, for fundamental equation:
given $S = A(n V U)^{\frac{1}{3}}$, find three state
equations, 350
 - 2, re-work example 1:
in energy representation, 351
- Examples VI-VIII
chapter VII, 318
- Exercise
I, chapter VIII, 350
- Exercise II-b, 17
- Exercises Chapter I
- 1a, 9
 - 1b, 13
 - 2a, 16
 - 2b, 17
- Exercises Chapter II
- 1, where 90 % molecules are in atmosphere
with decreasing temperature, 55
 - 2, total energy of column in atmosphere
with decreasing temperature, 55
- Exercises Chapter IV
- 1, work along
two adiabatic links, 135
 - 2, re-do example 11
for n objects, 174
 - 3, show: $\epsilon_{Heat Energy Pump}$
 $= 1 + COP$, 192
 - 4, show why T_f
must approach T_1 when $T_2 \rightarrow T_1$, 197
- Exercises Chapter V
- 1 to 6, 251
 - 1, prove: $\left(\frac{\partial t}{\partial p}\right)_s \left(\frac{\partial v}{\partial t}\right)_s =$
 $-v(\chi_t/\gamma)$, 251
 - 2, prove: $\left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial p}\right)_t =$

- $\left(\frac{C_p}{C_v}\right)$, 252
 3, re-do exercise 2
 by using Jacobians, 252
 4, prove: $(\chi_t - \chi_s) =$
 $t v \left(\frac{\alpha_p^2}{C_p}\right)$, 252
 5, prove: $\left(\frac{\partial L}{\partial v}\right)_s =$
 $-\left(\frac{\gamma}{v\chi_t}\right)\left(\frac{\partial t}{\partial p}\right)_s$, 253
 6, prove: $c_p =$
 $-\frac{1}{\mu}\left(\frac{\partial h}{\partial p}\right)_t$, 253
- Exercises Chapter VI
- show that figure 2b agrees with the Maxwell prescription, 271
 - for exact differential necessary that loop integral be vanishing but not sufficient, 273
 - question for skeptics, 282
- Exercises Chapter VIII
- show Callen rule also applies to entropy representation, 350
- Exercises Chapter X
- Maxwell relations
- for multi-constituent systems, 395
- Exotic form, 2
- Expansion
- virial Van der Waals gas, 260
- Experiment
- gedanken, 148
- Extensive, 30
- and intensive parameters, 30
- quantity, 30
- Extrema
- all types, 367
- energy minimum, 361
- entropy and energy occur simultaneously, 361
- entropy maximum, 357
- Helmholtz potential, 382
- Extremely Relativistic ideal gas, xi
- Extremum
- energy, 361
- entropy, 357
- Gibbs potential
- minimum at constant T and P , 387
- Helmholtz potential
- minimum at constant V and T , 382
- principle
- Gibbs free energy, 273
- Extremum Principles, x
- Extremum Principle
- for Gibbs potential, 387
- Fermi–Dirac and Bose–Einstein quantum gases., xi
- Figure
- Ia chap IV, pressure versus volume, 128
- Figure 1
- Chapter I, 10
- Figure 9: Dieterici isotherms, 302
- Figures Chapter I
- paths traveled, 10
- Figures Chapter III
- temperature versus volume ideal gas expansions: adiabatic, isothermal and isochoric, 93
 - ideal gas polytropics, 100
- Figures Chapter IV
- diesel cycle with ideal gas as working substance, 199
 - Otto cycle with ideal gas working substance, 202
 - Joule cycle with ideal gas working substance, 206
- 1a, pressure versus volume, 128
- 1b, temperature versus volume, 128
- 1c, temperature versus pressure, 128
- infinitesimal cycles added, 137
 - Carnot Cycle arbitrary working substance, 140
 - irreversible adiabatic process: entropy versus temperature, 146
 - schematic plot for example 2, 155
 - schematic plots for examples 5 and 6, 163
 - schematic plots for examples VIII and IX, 169
 - 8a, entropy difference versus T_2/T_1 , 195
 - 8b, total work versus T_2/T_1 , 195
 - 9, thermostats and isochores T versus V , 197
- Figures Chapter V
- entropy increase versus ratio pressures, 221

- 2, entropy increase versus (P_2/P_1) and (N_2/N_1) , 224
- Figures Chapter VI
 - 1a and 1b, hard core homogeneous pairs sphere of exclusion, 256
 - 2a, (p_o, v_o) plot of the Van der Waals isotherms for $t_o = 1.0$ and 0.9, 269
 - 2b, (p_o, v_o) plot of the Van der Waals isotherm for $t_o = 0.9$, 269
 - 3, (p_o, v_o) Van der Waals isotherms for $t_o = 1.0; 0.9; 0.8$, 274
 - 4, Van der Waals boundary of the metastable-unstable regions, 275
 - 5a, X_o as function of p_o for various fluids, 283
 - 5b, X_o as function of p_o , Van der Waals gas, 283
 - 6, reduced second virial coefficient, 285
 - 7, reduced molar densities, co-existent regime, 287
 - 8a, reduced vapor pressure in the co-existent regime and the PCS, 290
 - 8b, reduced vapor pressure in the co-existent regime, Van der Waals gas, 290
 - 9, Dieterici state equation isotherms for $t_o = 1.0, 0.9, 0.8, 0.7, 0.6$, 302
- Figures Chapter VII
 - 1, schematic view of Gay-Lussac-Joule apparatus, 304
 - 2, schematic view of Joule-Kelvin apparatus, 308
 - 3, schematic view of Joule-Kelvin's experiment results, 311
 - 4, constant enthalpy curves for nitrogen, 311
 - 5, Van der Waals reduced inversion temperature versus $(reduced\ volume)^{-1}$, 317
 - 6, Van der Waals reduced inversion temperature versus reduced pressure, 318
- Figures Chapter X
 - 1, phase boundaries
 - clausius–Clapeyron equation for non H₂O cases, 398
 - 2, phase boundaries Clausius–Clapeyron equation for H₂O, 399
- Finite sized interacting molecules, 256
- First law for quasi-static process, 213
- First $T.dS$ Equation, 215
- First and Second $T.dS$ Equations together, 234
- First and Second Laws, 212
- First Law, 212
 - for quasi-static process $t ds = du + p dv$, 213
 - is more than just energy conservation, 212
 - use of, 64
- First law, 152
- First Requirement intrinsic stability $C_V > 0$, 369
- First-Second Law Clausius version Differential Form, 212
- First-second law Clausius version, 152
- Flow
 - heat energy, 357
 - molecular, 359
 - isobaric-isothermal, 365
- Fluctuation metastable, 356
- Fluoride, 265
- Free Energy Helmholtz, 361
- Free energy Gibbs
 - extremum principle, 273
- Fundamental Equation and the equations of state, 337
 - for ideal gas energy representation, 349
 - for ideal gas, I, 346
 - the complete, ix
- Gas
 - perfect : model of, 23
 - nearly perfect, 306
 - reservoir in contact change in u and s , 238

- Gay-Lussac, Joseph Louis
(12/6/1778)
-5/9/1850), 303
- Gay-Lussac–Joule
experiment, ix
- Gay-Lussac-Joule (GLJ) coefficient, 304
- Gay-Lussac-Joule Coefficient
derivation, 305
description, 303
measurement, 304
perfect gas, 306
- Gedanken experiment, 148
gedanken experiment, 353
- Gibb's Free Energy, 384
- Gibbs
-Duhem relation
 energy representation, 345
 entropy representation, 345
free energy, 384
phase rule, 402
equation, 152
free energy
 extremum principle, 273
potential, 338, 341
potential and relative
 size of phases in single constituent
 system, 387
relationship
 \equiv first-second law, 213
specific potential: equal
 in coexistent phases, 388
- Gibbs Free Energy
decrease in
 constant mole-numbers, 386
equality of specific
 different phases, 388
- Gibbs phase rule, x
- Gibbs Potential
extremum principle, 387
helps determine
 enthalpy, 393
- Gibbs Potential Minimum
relative phase sizes, 387
- Gibbs, Josiah Willard
(2/11/1839)–(4/28/1903), 26
- Gibbs-Duhem, ix
relation:
 energy representation, 345
 entropy representation, 345
- Guggenheim, E. A
'thermodynamics'
 North Holland Publishing
 Company(1967), 287
- Guggenheim, E.A.
- J. chem Phys
 13, 253 (1945), 287
- Hamiltonian, 27
- Hard Core
 volume excluded,
 V_{excluded} , 257
 volume reduction
 Van der Waals gas, 256
- Hawking, Stephen, 211
- Heat
 caloric theory, 58
 energy, work and internal energy, 58
- Heat Energy
 specific, 63
- Heat Energy Flow
 always from hot to cold:
 why?, 357
 diathermic case, 357
- Heat Engines
 introductory remarks, 126
- Heat Of
 transformation, 390
- Heat transfer
 always increases entropy, 151
- Helium, 264
 liquid at 0.3 K, 398
- Helmholtz Free Energy, 361
 characteristic, independent
 variables: V and T , 380
 decrease in, 385
 decreases during
 spontaneous isothermal-isochoric
 processes, 382
 equality of specific
 for different phases, 383
 thermodynamics at
 constant V and T , 379
- Helmholtz Free energy, 381
- Helmholtz Potential
 helps determine
 internal energy, 392
- Helmholtz potential
 the Gibbs free energy
 and the enthalpy, x
- Helmholtz Potential Minimum
 relative size of phases, 383
- Helmholtz Thermodynamic Potential, 379, 380
- Hemmer, P. C.
 with Kac, M.
 and Uhlenbeck, G.E., 258
- Hess
 rules for chemo-thermal reactions, 88

- Hess' rules for chemo-thermal reactions, 57
- Hess, Germain Henri
(8/7/1802)
-(11/30/1850), 88
- Hydrogen
estimate inversion temperature, 320
number of atoms
in one gram, 4
sulfide, 264
- Ice
I, 399
Ice Point, 400
Ice-Point
estimate of temperature, 328
- Ideal Gas \equiv Perfect Gas, 34
- Identity
cyclic, 14
cyclic re-derived, 19
mixed, 20
simple, 20
useful, 19
- Independent
 p and v , 235
 t and v , 213
 t and p , 230
- Independent Variables
 p and v ; $u(p,v)$, 80
 t and p ; $u(t,p)$, 77
 t and v ; $u(t,v)$, 65
- Inert gases
Neon; Argon;
Krypton; Xenon, 283
- Inexact differential, 13
- Infinitesimal Carnot Cycles, 136
- Integrability Requirement, 12, 60
- Intemann, Robert, xii
- Intensive, 31
and extensive properties, 30
property, 31
- Inter-Particle
communication, 33
- Interacting
finite sized
molecules, 256
- Interaction
inter-particle, 4
- Interesting Relationships, 330
- Internal Energy
in non-interacting monatomic gases is
 $= \frac{3}{2} P V$, 122
state function, 78
perfect gas
see equation 2.27, 28
state function, 212
- Internal energy
and volume dependence
of C_v , 288
- Internal Energy and Enthalpy
measurement and related
examples, 303
- Internal Energy Minimum
and relative size
of phases, 374
- Internal Energy Minimum:
specific internal energy, 374
- Intra-molecular
vibrational rotational
motion, 35
- Intrinsic Stability
also, c_p and $\chi_S > 0$, 371
- Intrinsic Thermodynamic Stability
also requires $\left(\frac{\partial \mu}{\partial n}\right)_{S,V} > 0$, 371
requires c_v and $\chi_T > 0$, 367
- Introduction
and Zeroth law, 1
- Introductory Remark
chapter VII, 303
- Invariant Systems, 405
- Inversion Temperature
upper and lower, 317
- Irreversible process, 4
- Isenthalpic
curves of constant enthalpy, 311
Joule-Kelvin, 310
- Isentropic Processes, 236
- Isobaric
entropy flow, 364
- Isobaric Process, 3
- Isobaric-Isothermal
molecular flow, 365
- Isochoric process, 3, 69
- Isolated
adiabatically, 2
- Isothermal
Compression, 360
process, 8
- Isothermal compressibility
along critical isochore
just above T_c , 268
just below T_c , 280
- Isothermal Compression
upon contact, part with
lower pressure always shrinks: why?
from entropy max, 360

- lower pressure always shrinks: why?
 - use energy min., 365
 - volume exchange, 365
- Isothermal-Isobaric
 - molecular flow, 365
- Isothermal-Isochoric
 - change of state, 381
- Isothermally Stretched
 - ideal rubber, 244
- Isotherms
 - (p_o, v_o)
 - Van der Waals, 269
- Jacobian, 8
 - employed, 18
- Jacobian, Carl Gutav Jacob J.
 - (12/10/1804)
 - (2/18/1851), 252
- Jacobians: simple technique, 16
- Johannes Diderik Van der Waals, ix
- Joule
 - cycle, ideal gas engine, 206
 - Gay-Lussac coefficient
 - description, 303
 - measurement, 304
- Joule, James Prescott
 - (12/24/1818)–(10/11/1889), 58
- Joule, the unit, 58
- Joule-Gay-Lussac Coefficient
 - to the thermodynamic
 - temperature scale, 324
- Joule-Kelvin
 - coefficient
 - for nearly perfect gas: calculation, 313
 - for perfect gas: calculation, 313
 - for Van der Waals gas: calculation, 314
 - for Van der Waals gas: inversion point, 315
 - positive and negative regions, 315
 - coefficient:
 - constant enthalpy, 308
 - description, 308
 - effect: derivation, 312
- Joule-Kelvin Coefficient
 - constant enthalpy, 308
 - description, 308
 - for nearly perfect gas:
 - calculation, 313
 - for perfect gas:
 - calculation, 313
 - for Van der Waals gas:
 - calculation, 314
 - inversion point, 315
 - positive and negative regions, 315
 - to the thermodynamic
 - temperature scale, 326
- Kac, Mark
 - (8/3/1914-10/26/1984), 258
- Kamerlingh-Onnes, Heike
 - (9/21/1853-2/21/1926), 260
- Kelvin, 31
 - temperature scale
 - Carnot temp scale, 131
- Kelvin, Lord:
 - born William Thomson
 - (6/26/1824)–(12/17/1907), 131
- Kelvin-Planck
 - entropy always increases
 - in irreversible-adiabatic process, 146
- Kindling, 57
- Klein, M. J.
 - Van der Waals
 - centennial conference (1974), 257
- Krypton, 264, 283
- Langevin paramagnet, xi
- Laplace, Pierre-Simon
 - (3/23/1749)–(3/5/1827), 255
- Large numbers
 - most probable state,
 - thermodynamics, 4
- Latent Heat
 - of vaporization of water, 90
- Law
 - second, Carnot version, 141
 - second, Clausius version, 142
 - second, Kelvin-Planck, 145
 - zeroth
 - re-confirmation, 363
- Laws
 - first and second, 212
- Laws of Thermodynamics
 - second, 62
 - first, 62
 - zeroth, revisited, 354
- Laws of thermodynamics
 - Carnot leads to Clausius, 142
 - second, Carnot version, 135, 141
 - second, Clausius version, 142
 - second, Kelvin-Planck, 145
 - zeroth, 4
- Le Châtelier principle, x
- Le Châtelier's Principle, 366
- Lebovitz, Joel L.

- Rutgers University, 258
- Legendre Transformation, 377, 379
- Legendre Transformations
 - Clausius–Clapeyron
 - Gibbs phase rule, 373
- Legendre transformations, x
- Lever rule, 281
- Liquid, 2
- Liquid to gas
 - transition
 - and vice versa, 282
- Location
 - of internal energy, 62

- Macroscopic
 - systems, 4
- Mass of carbon-12 atom, 5
- Massieu Functions, 377
- Mathematical procedures, 8
- Maximum
 - available work, 380
- Maximum Available Work, 380
 - equals, resulting decrease
 - in Helmholtz potential, 381
 - isothermal-isobaric
 - change of state, 385
 - non-PdV variety
 - equals corresponding decrease of Gibbs potential, 386
- Maximum Entropy
 - in adiabatically isolated
 - systems: general statement, 375
- Maxwell
 - relations, 393
 - construction, 269
 - prescription, thermodynamic justification, 269
 - prescription: alternate justification, 272
- Maxwell prescription
 - alternate justification, 272
- Maxwell, Clerk
 - relations, 393
- Maxwell, J. Clerk
 - (6/13/1831)
 - (11/5/1879), 258
 - (6/13/1831-11/5/1879), 26
- Mayer's Cluster
 - expansion, xi
- Mayer, Joseph Edward
 - (2/5/1904-10/15/1983) virial expansion, 261
- Measurement
 - chapter VII, 304

- Meta-Stable
 - equilibrium, 395
- Meta-Stable Equilibrium, x
- Metal Rod
 - equation of state, 247
- Metastable Fluctuation, 356
- Metastable-unstable regions
 - Van der Waals, 275
- Methane, 265
- Minimum Internal Energy
 - in adiabatically
 - isolated systems, 374
- Mitsubishi, GDI engine, 205
- Mixed identity, 20
- Mixing Ideal Gas
 - different temperature, pressure and number
 - of atoms
 - entropy change, 225
 - isothermal, different pressures
 - same number atoms, 219
 - isothermal, different pressures and number
 - of atoms
 - entropy change, 222
- Mixture of Perfect Gases
 - temperature and pressure, 35
- Model
 - perfect gas, 23
- Moduli
 - bulk and elastic, 103
- Molar
 - specific volumes
 - and densities, 276
- Molar densities
 - of co-existing phases, 287
 - reduced, 287
- Mole
 - numbers, 26
 - one mole has N_A particles, 69
- Molecular Flow
 - at constant T and P ,
 - always from higher chemical potential
 - to lower: why?, 359
 - isothermal-isobaric
 - away from regions with larger, to
 - regions with smaller chemical potential, 365
- Molecule
 - finite sized
 - and interacting, 256
- Monatomic, 92
- Mono-Variant Systems, 406
- Most probable
 - occurrence, 4
 - state; thermodynamics,

- large numbers, 4
- Motive Forces, 353
 - direction of, 357
 - energy formalism, 364
 - entropy formalism, 357
- Multi-Phase
 - multi-constituent systems, 402
- Multiple-Component Systems, 341

- Negative Temperature
 - cursory remarks, 335
- Negative temperature
 - cursory remarks, 209
- Neon, 264, 283
- Newton
 - bravo, 238
 - velocity of sound, 237
- Newton's Law Of Cooling, 120
- Newton, Isaac
 - (1/4/1643)
 - (3/31/1727), 120
- Nitric oxide, 265
- Nitrogen, 264
- Non-Carnot heat cycle, 148
- Normalized Average, 27
- Notation
 - description, 63
- Notation: Chapter I, 11
- Nye, Edwin P., 282
 - and Dillio, Charles C, 282

- Object, 1
- Otto cycle, 202
- Otto, Nicolaus
 - (6/14/1832)
 - (1/26/1891), 202
- Oxidation
 - C to CO
 - to CO₂, 89
- Oxygen, 264
- Ozone
 - dissociating, 48

- Paddles, Churning, 59
- Partial Pressure
 - of mixtures,
 - example I, chap II, 47
- Partial Pressures
 - dalton's law, 36
- Pascal
 - principle, 356
- Pascal's Law, 24, 31
- Pascal, Blaise
 - (6/19/1623)
 - (8/19/1662), 356
- Pathria, R. K., xii
- PCS
 - principle of
 - corresponding states, 282
- PdV
 - non pdv work, 386
- PdV Work, 386
- Pedagogical benefit, vii
- Perfect Gas
 - $C_p \equiv c_p \equiv n c_p \equiv n C_p$, 34
 - $C_v \equiv c_v \equiv n c_v \equiv n C_v$, 34
 - \equiv ideal gas, 34
 - adiabatics, 91
 - atmosphere, 38
 - dalton's law of partial pressures, 36
 - diatomic, 35
 - equation of state – see equation 2.28, 30
 - extremely relativistic particles: compare
 - result with equation 2.31, 46
 - for mixtures average translational kinetic
 - energy of all molecules is equal, 37
 - for mixtures equations 2.41, 2.42 and 2.43
 - hold, 37
 - fundamental equation
 - energy representation, 349
 - fundamental relation
 - entropy representation, 346
 - internal Energy U, 28
 - Joule-Kelvin
 - coefficient: calculation, 313
 - known equations
 - of state entropy representation, 344
 - model of, 23
 - monatomic, 34
 - monatomic and diatomic, 34
 - polytropics, 99
 - thermodynamic equilibrium
 - attainment of, 33
 - thermodynamic scale
 - for temperature, 328
 - three state equations
 - energy representation, 349
 - entropy representation, 348
- Perfect gas
 - atmospheres, 23
 - Carnot cycle, 133
 - Stirling cycle, 197
- Perpetual Machine
 - first kind, 62
- Perpetual machine

- second kind, 126
- Phase Equilibrium
 - relationships, 403
 - number of relationships, 404
 - relationships and
 - the phase rule, 405
 - the variance, 405
- Phase Rule
 - for systems with internal chemical reactions, 406
- Phase Transformations, 390
- Pippard, 5
- Pippard, Alfred Brian
 - (9/7/1920)
 - (9/21/2008), 5
- Planck, Max
 - (4/23/1858)-(10/4/1947), 145
- Poisson Equations, 92
- Polytropics
 - ideal gas, 57
- Potentia
 - Gibbs, 338
- Potentials
 - thermodynamic:
 - s, f, g and h , 391
- Pound, R. V., 210
- Pound, Robert Vivian
 - (5/16/1919-4/12/2010), 336
- Preface, vii
- Prescription, Maxwell
 - thermodynamic justification, 269
- Pressure
 - monatomic Perfect Gas, 24
- Pressure at Constant v ,
 - $\propto t$, then c_v
 - independent of v , 218
- Principle
 - of corresponding states: PCS , 282
- Procedure
 - establish inter-relationships, 64
- Process
 - equilibrating, 33
 - isochoric, 69
 - isentropic, 236
 - isobaric, 3
 - isochoric, 3
 - isothermal, 8
 - quasi-static, 3
 - reversible does not imply local isentropy, 130
 - reversible implies global isentropy, 130
 - reversible,
 - irreversible, 4
- Proof of Equation 10.76, 403
- Prove $C_p = \frac{v\chi_t}{\mu} \left(\frac{\partial h}{\partial v} \right)_t$, 332
- Prove $\left(\frac{\partial h}{\partial t} \right)_v = C_p(1 - \mu \alpha_p / \chi_t)$, 333
- Prove $\left(\frac{\partial u}{\partial s} \right)_v = t$, 335
- Prove $\left(\frac{\partial t}{\partial p} \right)_h - \left(\frac{\partial t}{\partial p} \right)_s = - \left(\frac{v}{C_p} \right)$, 331
- Prove $\left(\frac{\partial t}{\partial v} \right)_u - \left(\frac{\partial t}{\partial v} \right)_s = \left(\frac{p}{C_v} \right)$, 330
- Prove $\left(\frac{\partial u}{\partial v} \right)_s = -p$, 335
- Prove $C_v = \frac{1}{\eta v \chi_t} \left(\frac{\partial u}{\partial p} \right)_t$, 333
- Pump
 - Carnot heat energy, 190
- Purcell, E. M., 210
- Purcell, Edward Mills
 - (8/30/1912-3/7/1997), 336
- Q.E.D.
 - \equiv Quod Erat Demonstrandum which was to be proven, 49
- Quasi-Static
 - adiabatic work equals change in internal energy, 96
 - process, 59
- Quasi-static
 - process is often but not necessarily reversible, 128
- Quasi-static process, 3
- Question for skeptics, 282
- R, molar gas constant
 - $= 8.314472(15)$
 - $\text{J mol}^{-1} \text{K}^{-1}$, 27
- Ramsey, Norman Foster
 - (8/27/1915)
 - (12/7/1993), 209
- Rarefaction and Compression, 237
- Re-confirmation
 - zeroth law, 363
- Re-derived
 - cyclic identity, 19
- Reaction Enthalpy, 83
- Realistic engines
 - idealized version, 199
- Rectilinear diameters

- principle of, 278
- Reduced
 - equation of state Van der Waals gas, 264
- Reduced vapor pressure
 - co-existent regime and the PCS, 289
- Refrigerator, 142
- Refrigerator or air-conditioner
 - Carnot, 185
- Relations
 - Maxwell, 393
- Relationships
 - some, interesting, 330
- Relative Size of Phases
 - such that
 - entropy is maximum, 376
- Remark, 351
- Representation
 - energy, 343
 - entropy, 343
- Requirement
 - integrability, 12
- Reversible process, 4
 - is globally isentropic, 128
 - is quasi-static, 128
- Reversible-Adiabatic
 - entropy stays constant, 147
- Rhines, Frederick, 281
- Richardson Effect, xi
- Riseborough, Peter, xii
- Rule
 - Callen, 342
 - the lever, 281
- Rumford
 - Benjamin Thompson
 - Count of Bavaria (3/26/1753)–(8/21/1814), 58
- Salinger, G. L.
 - Addison-Wesley Publishers
 - Third Edition, (1986), xii
- Schroeder, D. V.
 - introduction thermal physics
 - Addison-Wesley-Longman, 291
- Sears and Salinger
 - op. cit., 399
- Sears, F. W.
 - Addison-Wesley Publishers
 - Third Edition, (1986), xii
- Second $T.dS$ Equation, 231
- Second and First Laws, 212
- Second law
 - Carnot statement, 135
 - Clausius statement, 142
 - Kelvin-Planck statement, 145
 - statement, 141
- Second Requirement
 - intrinsic stability
 - $\chi_T > 0$, 370
- Show $\left(\frac{\chi_T}{\chi_S}\right)$
 - $= 1 - \left(\frac{\alpha_p}{\alpha_s}\right)$, 241
- Show $\left(\frac{v}{C_p}\right)$
 - $= \left(\frac{\partial t}{\partial p}\right)_s - \left(\frac{\partial t}{\partial p}\right)_h$, 243
- Show $C_p \left(\frac{\partial L}{\partial s}\right)_h$
 - $= t - \alpha_p t^2$, 242
- Simple identity, 20
- Simple System, 378
- Single Constituent Systems
 - Helmholtz potential minimum:
 - specific Helmholtz potential equal, 383
 - internal energy minimum:
 - in isolated systems, 374
 - relative size of phases
 - are those that yield lowest Helmholtz potential, 383
- Single-Component Systems, 341
- Solid, 2
- Solutions, important to read, vii
- Some definitions, 1
- Sound
 - velocity, Newton's treatment, 237
- Specific Heat, 63
 - SI units, 64
- Specific heat
 - enthalpy, η and μ
 - Van der Waals Gas, 293
- Specific Heat Energy, 65
- Specific Internal Energy
 - is equal, 376
- Spinodal curve, 275
 - Van der Waals, 275
- Spontaneous Process
 - isothermal-isobaric
 - occurs with decrease in Gibbs potential, 387
 - isothermal-isochoric
 - occurs with decrease in Helmholtz potential, 382
- Spontaneous process
 - increases total entropy, 145
- Stability
 - thermodynamic, 366
- Stable
 - thermodynamic equilibrium, 367

- Stanley, H.E.
 phase transitions
 and critical phenomena Oxford
 University Press(1971), 283
- State
 equation of, 8, 9
 equations of, 342
 function, 30, 59
 function and variables, 14
 variable, 9
 variables, 30
- State Function
 enthalpy h ; internal energy u , 78
- State function
 entropy, 138
- Statistical Approach
 temperature, 26
- Statistical mechanics, vii
- Stirling cycle
 ideal gas working substance, 197
- Stirling, Robert
 (10/25/1790)
 -(6/6/1878), 197
- Su, G.J.
 (1946), 283
- Sub-Systems
 in mutual equilibrium, 354
- Summary, 372
- Susceptibility
 isentropic and isothermal, 253
- t and p , Independent
 $u(t,p)$, 77
- Table
 Van der Waals gas
 critical constants, 264
- Temperature
 $T \text{ K} = T \text{ }^\circ\text{C} + 273.15$, 132
 a statistical approach, 26
 celsius, 32
 empirical, 5, 7
 from empirical
 to thermodynamic, 322
 ice-point, 32
 ideal gas
 thermodynamic scale, 328
 Kelvin scale
 \equiv absolute scale, 131
 negative, cursory remarks, 209, 335
 steam point, 32
 thermodynamic approach, 31
 thermodynamic scale via
 the Joule-Gay-Lussac coefficient, 324
 the Joule-Kelvin coefficient, 326
- Temperature and Pressure
 mixture of perfect gases, 35
- Temperature change
 on mixing
 Van der Waals Gases, 290
- Temperature of Ice-Point
 an estimate, 328
- ter Haar
 D. and Wergeland, H., 209
 for negative temperature
 energy must have upper-bound, 210
- ter Haar, Dirk, 9
 (4/22/1919)–(9/3/2002), xii
 op. cit, 336
- The PdV Work, 386
- Thermal equilibrium, 3
 mutual, 7
- Thermo-Motive Force
 internal energy, 361
- Thermodynamic
 equilibrium
 attainment of for a perfect gas, 33
 potentials:
 s , f , g and h , 391
 system, 1
- Thermodynamic Equilibrium
 stable, 367
- Thermodynamic justification
 Maxwell Prescription
 alternate analysis, 272
 Maxwell prescription
 first analysis, 269
- Thermodynamic Motive Forces
 direction of, 357
 direction of entropy formalism, 357
 energy formalism, 361
 I, entropy extremum, 357
 II, energy extremum, 361
- Thermodynamic Phases, x
- Thermodynamic Potentials
 Clausius–Clapeyron
 Gibbs phase rule Legendre
 transformations, 373
- Thermodynamic Stability, 353
 intrinsic
 requires C_V and $\chi_T > 0$, 367
 intrinsic requires
 c_v and $\chi_T > 0$, 367
 requires positive
 c_v and χ_t , 216
 section on, 366
- Thermodynamic Temperature
 scale via

- the Joule-Kelvin coefficient, 326
 - via Joule-Gay-Lussac coefficient, 324
- Thermodynamics
 - classical, A. Brian Pippard, 5
 - first law, 62
 - large numbers,
 - most probable state, 4
 - second law Carnot version, 135
 - zeroth law, 4
 - Third $T.dS$ Equation, 236
 - Third Requirement
 - intrinsic stability
 - $\left(\frac{\partial \mu}{\partial n}\right)_{S,V} > 0$, 371
 - Thompson, Benjamin
 - Count Rumford of Bavaria (3/26/1753)–(8/21/1814), 58
 - Total differential, 9
 - Total entropy
 - increases by spontaneous processes, 145
 - Transformation
 - heat of, 390
 - Legendre, 377, 379
 - Transition
 - from liquid to gas and vice versa, 282
 - Triple and Ice Points
 - of water: why different?, 400
 - Triple Point, 400
 - Triple point
 - of pure water, 33
 - Two phase region
 - Van der Waals, 262
- Uhlenbeck, George Eugene (12/6/1900-10/31/1988), 258
- Units
 - molal, 259
- Useful identities, 19
- Van der Waal's Gas
 - energy and entropy change, 246
- Van der Waals
 - behavior below T_c , 269
 - critical point, 262
 - critical region, 265
 - equation as a cubic, 263
 - equation of state
 - for a mixture, 260
 - equation of state for 1 mole, gas or liquid:
 - $(p + \frac{a}{v^2})(v - v_{\text{excluded}}) = RT$;
 - $p \equiv P, v = \frac{V}{n}$, 259
 - equation of state for n moles, gas or liquid:
 - $(P + \frac{an^2}{V^2})(V - V_{\text{excluded}}) = nRT$, 259
 - equation of state in reduced form, 260
 - parameters from critical constants, 264
 - reduced equation of state, 264
 - theory of imperfect gases, 255
 - two phase region, 262
 - virial expansion, 260
- Van der Waals Gas
 - equation of state, 71
 - Gay-Lussac-Joule coefficient, 307
- Van der Waals gas
 - adiabatic state equation
 - above critical point, 297
 - reduced vapor pressure, 290
 - specific heat
 - enthalpy, η, μ , 293
 - work done
 - entropy, internal energy change, 296
- Van der Waals gases
 - temperature change
 - on mixing, 290
- Van der Waals theory of imperfect gases, 255
- Van der Waals, Johannes Diderik (11/23/1837)–(3/18/1923), 255
- Variable
 - state, 9
- Variance
 - phase equilibrium relationships, 405
- Velocity of Sound
 - Newton's treatment, 237
- Vibrational rotational motion
 - intra-molecular, 35
- Violation
 - of Carnot version leads
 - to Clausius version, 142
- Virial coefficient
 - reduced second, 285
 - second, changes sign at Boyle temperature, 262
 - second, changes sign at Boyle temperature, 262
- Virial expansion
 - Van der Waals gas, 260
- Walls

- conducting, 2
- diathermal, 2
- Wergeland, H., xii, 9
- Work done
 - entropy, internal energy change, 296
- Work to Heat Energy, 61

- Xenon, 264, 283

- Zemanski, M. W.
 - Dittman, R. H.
 - 'Heat and Thermodynamics', McGraw Hill, 1981., 311
- Zemansky, M. W.
 - 'Heat and Thermodynamics' McGraw Hill(1981), 311
- Zeroth Law
 - reconfirmation, 363
 - revisited, 353
 - section, 31
- Zeroth law, viii
 - assertion, 7
 - introduction and, 1
 - motive forces and stability, 8
 - of thermodynamics, 4